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A Study by Infrared Analysis of the Oxidation of 1-Phenyl-3-Pyrazolidone–Hydroquinone Developers . *G. F. Van Veelen and H. Ruysschaert* 129

The Effect of Film Thickness Variations on Coherent Light • *Arthur L. Ingalls* 135

A High-Speed Color Printer • *A. M. Gundelfinger, E. A. Taylor, and R. W. Yancey* 141

A Novel Method for Characterizing Photographic Gelatin • *F. W. H. Mueller and C. B. Roth* 151

A Demonstration of Color Perception with Abridged Color-Projection Systems • *C. S. McCamy* 155

The Bromination of Gelatin • *Walter Cooper* 160

Photographic Developing Agents: 2. Quinones *R. W. Henn, J. F. Tinker, and H. L. Fielding* 167

An Approach to Monobath Kinetics • *R. E. Swing and S. A. Barry* 173

Notes from the Editor 175

Discussion and Evaluation 176

Book and Journal Reviews 178

New Products and Developments • *Frank Smith* 183

RAPID PROCESSING SYMPOSIUM ANNOUNCEMENT 150

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PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 4, Number 3, May-June 1960

A Study by Infrared Analysis of the Oxidation of 1-Phenyl-3-Pyrazolidone–Hydroquinone Developers

G. F. VAN VEELEN AND H. RUYSSCHAERT, *Research Department, Gevaert Photo-Producten N. V., Mortsel, Belgium*

1-Phenyl-3-pyrazolidone can be extracted quantitatively from PQ developers with chloroform. The infrared spectrum of the extract shows at 5.85 μ a strong carbonyl band, which can be used for quantitative analysis. By means of the spectrum, a study has been made of the oxidation by air of PQ developers. When hydroquinone or sodium hydroquinone monosulfonate are present together with sulfite, 1-phenyl-3-pyrazolidone is almost quantitatively regenerated. In the absence of sulfite, 1-phenyl-3-hydroxypyrazole is immediately formed, as can be proved by the infrared spectrum.

Since we could not get reproducible results by the iodometric determination of 1-phenyl-3-pyrazolidone, proposed by A. J. Axford,[1] we investigated other methods of analysis based upon infrared spectra.

The infrared spectrum of 1-phenyl-3-pyrazolidone shows a very intense band at 5.85 μ (C=O stretching vibration). The extinction of this band can be used for a quantitative determination of the concentration of 1-phenyl-3-pyrazolidone in chloroform extractions of PQ (1-phenyl-3-pyrazolidone–hydroquinone) developers.

After we had completed our study, G. I. P. Levenson, at a meeting of the Royal Photographic Society of London in December 1958, proposed a modified method of analysis, also based upon chloroform extraction. However, the 1-phenyl-3-pyrazolidone is still titrated iodometrically in the extract. A description of this method has recently appeared.[2]

By oxidation of 1-phenyl-3-pyrazolidone, 1-phenyl-3-hydroxypyrazole is formed which does not exhibit in its infrared spectrum the aforementioned C=O band,* but shows, however, an intense band at 6.46 μ, which is absent in 1-phenyl-3-pyrazolidone. Hence, infrared analysis allows us to examine the circumstances under which 1-phenyl-3-pyrazolidone is regenerated in PQ developers and also to detect the presence of 1-phenyl-3-hydroxypyrazole in oxidized developers.

Analytical Procedure

The analysis of 1-phenyl-3-pyrazolidone is worked out for PQ developers. However, the infrared analysis is in principle applicable to all 1-phenyl-3-pyrazolidone-containing developers, on condition that other carbonyl-containing products are absent; superposition of these additional C=O frequencies falsify the calculation of the 1-phenyl-3-pyrazolidone concentration.

1-Phenyl-3-pyrazolidone is quantitatively extracted from the developer with chloroform. In addition, chloroform is practically transparent in the spectral region important to the analysis.

The extraction is done at pH 8. Under these circumstances, some hydroquinone will be extracted too. In order to obtain the same background absorption for all determinations, the extract is always saturated with hydroquinone.

Figure 1 clearly illustrates that this can be done because the spectrum of hydroquinone has very little influence on the C=O stretching frequency of 1-

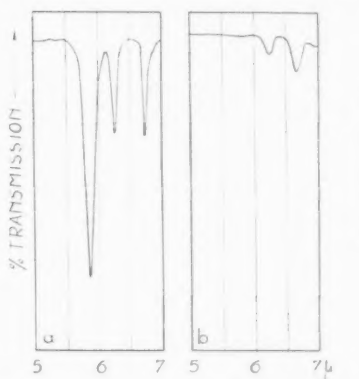


Fig. 1. (a). Infrared spectrum of 1-phenyl-3-pyrazolidone in chloroform solution (3 mg/ml); cell thickness, 0.5 mm. (b) Infrared spectrum of hydroquinone in saturated chloroform solution; cell thickness, 0.5 mm.

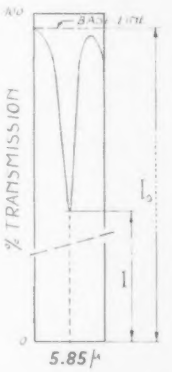


Fig. 2. The baseline method.

Received 8 October 1959.

1. A. J. Axford, *Phot. Eng.*, **7**: 23 (1956).
2. G. I. P. Levenson and N. G. Rumens, *J. Phot. Sci.*, **7**: 38 (1959).

* Apparently, in chloroform, the keto-enol equilibrium, pyrazolone ⇌ hydroxypyrazole, is completely shifted to the enol form.

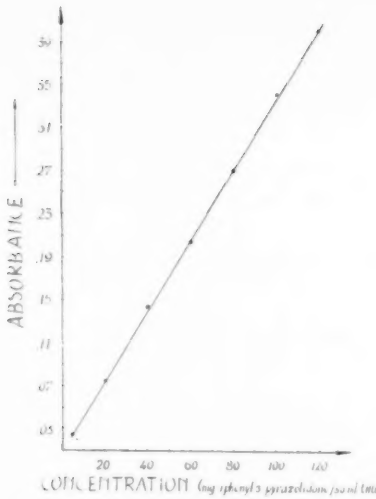


Fig. 3. Calibration curve for quantitative determination of 1-phenyl-3-pyrazolidone.

phenyl-3-pyrazolidone. Moreover, any disturbing effect caused by hydroquinone is compensated by a hydroquinone saturated chloroform solution in the reference cell.

The determination is done on a double-beam spectrophotometer following the base line method. As illustrated in Fig. 2, a horizontal line drawn from the minimum at 5.5 μ has been chosen as base line. The values I_0 and I are measured from the 0% transmission line, respectively, to the base line and to the minimum transmission of the carbonyl-stretching band at 5.85 μ.

The calculated absorbance, log I_0/I, is plotted as a function of the concentration in Fig. 3. A linear relationship was found within the concentration region from 5 to 120 mg 1-phenyl-3-pyrazolidone in 50 ml chloroform solution. The concentration of the chloroform extract should fall within the linear part of the calibration curve. This can be arranged for by adjusting the volume of the developer which is to be extracted by chloroform.

Experimental Procedure

(1) The infrared apparatus used for the quantitative analysis is a Perkin-Elmer double-beam spectrophotometer, Model 21, equipped with a sodium chloride prism. In practice, any type of double-beam apparatus can be used for the described analysis.

The apparatus is set on the following characteristics:

Response	1:1
Gain	5.5
Speed	3.5
Suppression	0
Scale	5 cm/μ

The spectrum is measured between 5.5 μ and 6.2 μ with a constant instrument slit-width of 0.096 mm. The adjustment of the 0% and 100% transmission line is made without cells in the two beams at the wavelength of the maximum absorption of the carbonyl band (5.85 μ). The solutions are measured in sealed calcium fluoride cells with a path length of 0.5 mm.

(2) In a study of the oxidation of 1-phenyl-3-pyrazolidone, we needed the complete spectrum between 5 and 15 μ. Therefore the chloroform extracts were completely evaporated and the residue studied with the well-known potassium bromide technique. As will be described later, the product formed was 1-phenyl-3-hydroxypyrazole, which was determined quantitatively by measuring the intensity of the absorption band at 6.46 μ after extraction by methylene chloride. In this region, chloroform cannot be used because of its own absorption. Methylene chloride is sufficiently transparent at 6.46 μ.

(3) The required chemicals for the quantitative analysis are:

6 N sulfuric acid
Phenolphthalein
Chloroform p.a.

(4) *Procedure for quantitative analysis:* A known amount of developer, containing 10 to 100 mg of 1-phenyl-3-pyrazolidone, is brought into a separating funnel. The volume is made up to 50 ml. Some drops of phenolphthalein are added, and 6 N sulfuric acid is then added until the indicator is decolorized. The volume is extracted three times with about 15 ml of chloroform. The three extracts are collected in one receiver. After saturation with hydroquinone, the solution is filtered into a 50-ml graduated flask and made up to volume with chloroform. The extinction at 5.85 μ is measured against a reference cell containing a saturated hydroquinone solution. The amount of 1-phenyl-3-pyrazolidone is read on the calibration curve.

(5) *Results:* The following developer formulation was analyzed:

Sodium hexametaphosphate	1 gram
Sodium sulfite (anhydrous)	60 grams
Sodium carbonate (anhydrous)	30 grams
Potassium bromide	1 gram
Hydroquinone	5 grams
1-phenyl-3-pyrazolidone	different quantities (see tabulation below)
Water	up to 1 liter

Amount in grams of 1-phenyl-3-pyrazolidone/liter:

Added	Analyzed					Average
0.200	0.190	0.204	0.200	0.200	0.194	0.198
2.00	2.00	1.98	1.94	2.04	1.84	1.96

TABLE I

	Solution number								
	1	2	3	4	5	6	7	8	9
1-Phenyl-3-pyrazolidone	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Hydroquinone	——	——	4.4	4.4	——	——	0.4	——	——
Hydroquinone monosulfonate	——	——	——	——	9	——	——	0.9	2.7
Hydroquinone disulfonate	——	——	——	——	——	13.8	12.4	12.4	9.7
Sodium carbonate	20	20	20	20	20	20	20	20	20
Sodium sulfite	——	40	——	40	40	40	40	40	40

Oxidation of PQ Developers

The infrared method of analysis allowed us to investigate the oxidation of PQ developers by air.

In fresh PQ developers, 1-phenyl-3-pyrazolidone is quantitatively regenerated by hydroquinone.[3] Only in developing solutions that are heavily oxidized is 1-phenyl-3-pyrazolidone irreversibly transformed into the corresponding hydroxypyrazole.

The determination of the 1-phenyl-3-pyrazolidone in the chloroform extracts of the developers and the potassium bromide spectra of the evaporated extracts (Fig. 4a, b and c) can inform us whether 1-phenyl-3-pyrazolidone is regenerated or 1-phenyl-3-hydroxypyrazole is formed. In some experiments, we have made a quantitative analysis of the hydroxypyrazole formed. For that purpose, we used the absorption band at 6.46 μ of the hydroxypyrazole in methylene chloride as described under *Experimental Procedure*.

Nine different developing baths were oxidized by air bubbling. The temperature was 22° ± 1°C. The composition in grams per liter of the solutions is as indicated in Table I. The pH has been adjusted to 10.0 in all cases. At intervals samples have been taken for analysis. The tabulated values are an average of several oxidation runs.

3. A. J. Axford and J. D. Kendall, *Proc. Roy. Phot. Soc. Conference*, London, 1953, p. 169.

Results

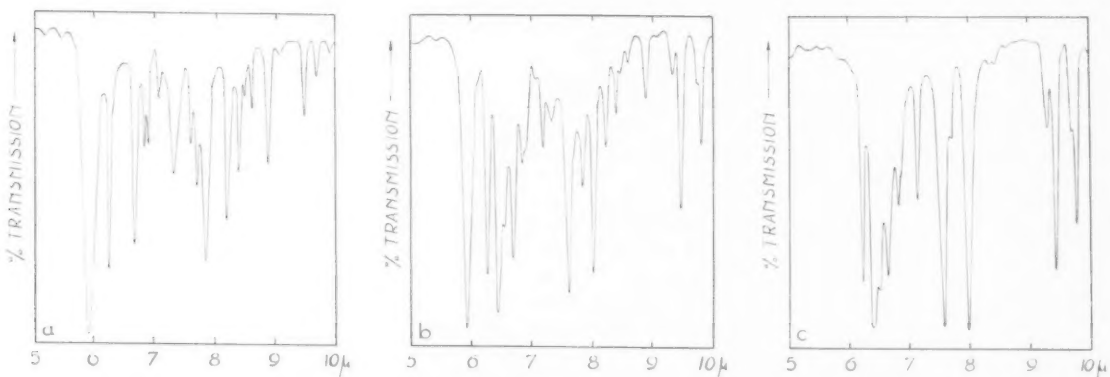
Solution No. 1

Time of oxidation, hours	Color	1-Phenyl-3-pyrazolidone,* g/l	1-Phenyl-3-hydroxypyrazole,** g/l	pH	Spectrum***
0	Orange	1.10	——	10.0	——
½	Red	0.81	——	——	Mixed spectrum of pyrazolidone and hydroxypyrazole
1	Purple	0.43	——	——	——
2	Purple	0	1.41	9.5	only hydroxypyrazole

* Calculated from C=O absorption in chloroform at 5.85 μ.

** Calculated from the absorption in methylene chloride at 6.46 μ.

*** The spectrum has been taken in KBr between 5 μ and 10 μ as described before.



(a) Infrared spectrum of 1-phenyl-3-pyrazolidone.

(b) Infrared spectrum of an extract containing 1-phenyl-3-pyrazolidone and 1-phenyl-3-hydroxypyrazole.

(c) Infrared spectrum of 1-phenyl-3-hydroxypyrazole.

Figure 4

Solution No. 2

Time of oxidation, hours	Color*	Sodium sulfite,** g/l	1-Phenyl-3-pyrazolidone, g/l	1-Phenyl-3-hydroxypyrazole, g/l	pH	Spectrum
0	Pink	40	1.39	——	10.0	——
1	Pink orange	——	0.74	——	——	——
2	Yellow orange	38	0.30	——	10.0	Mixed spectrum. See Fig. 4b
3	Faint yellow	38	0.06	——	——	——
4 1/2	Colorless***	38	0	0.80	9.9	——

* The absorption spectrum in the visible region has a maximum at 516 mμ; this maximum is characteristic for the presence of an intermediate oxidation product of phenylpyrazolidone; the final product 1-phenyl-3-hydroxypyrazole is colorless.
** Titrated iodometrically.
*** The solution becomes colorless, contrary to Solution No. 1.

Solution No. 3

Time of oxidation, min	Color	Hydroquinone,* g/l	1-Phenyl-3-pyrazolidone, g/l	pH	Spectrum
5	Brown	4.4	1.10	10.0	Hydroxypyrazole begins to form
20	Brown	4.1	0.59	——	Mixed spectrum with strong hydroxypyrazole bands
30	Brown	3.8	0.10	——	——
50	Brown	3.7	0	9.5	——

* Titrated cerimetrically.

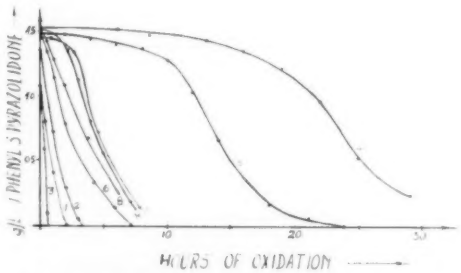


Fig. 5. Graphical illustration of the regeneration and oxidation of 1-phenyl-3-pyrazolidone in the examined solutions.

Figure 5 illustrates the regeneration and oxidation of 1-phenyl-3-pyrazolidone in the nine solutions.

Solution No. 4

Time of oxidation, hours	Color	Hydroquinone, g/l	Hydroquinone sulfonates,* g/l	1-Phenyl-3-pyrazolidone, g/l	Sodium sulfite, g/l	pH	Spectrum
0	Colorless	4.14	0.5	1.55	39	10.0	——
6	Pale yellow	0.29	7.6	1.54	32	——	No hydroxypyrazole
8 1/2	Yellow	0	——	1.48	27	10.4	——
13	Yellow	0	8.6	1.45	26	——	——
16	Orange yellow	0	8.8	1.35	26	——	——
19	Orange red	0	8.8	1.26	26	——	Weak hydroxypyrazole band
22	Orange red	0	——	0.96	——	10.8	——
25	Orange red	0	——	0.53	——	——	Mixed spectrum
29	Orange red	0	9.0	0.25	——	——	——
33	Orange red	0	——	0.02	——	——	Weak pyrazolidone band

* Determination by ultraviolet analysis.[4] Hydroquinone monosulfonate has a maximum absorption at 300 mμ, the disulfonate at 310 mμ. The difference between the two spectra is too small to allow a quantitative analysis of the two forms. Column 4 gives an estimation of the sum of the mono- and disulfonates.

4. J E. Lu Valle, *J. Am. Chem. Soc.*, **74:** 2974 (1952).

Solution No. 5

Time of oxidation, hours	Color	Hydroquinone monosulfonate, g/l	1-Phenyl-3-pyrazolidone, g/l	1-Phenyl-3-hydroxypyrazole, g/l	Sodium sulfite, g/l	Sodium sulfate,* g/l	pH
0	Colorless	8.8	1.51	——	40	——	10.0
2	Pale yellow	——	1.49	——	——	——	——
4	Yellow	——	1.44	——	——	——	——
6	Yellow	——	1.41	——	32	——	——
8	Orange yellow	——	1.39	——	——	——	——
10	Orange	——	1.30	none	26	——	10.3
12	Red	——	1.01	——	25	——	——
14	Red	——	0.65	0.34	24	15	10.7
18	Red	——	0.16	——	20	——	——
21	Red	——	0.07	——	——	——	——
24	Red	——	0	1.02	——	——	——

* Determined as barium sulfate.

Solution No. 6

Time of oxidation, hours	Color	Hydroquinone disulfonate, g/l	1-Phenyl-3-pyrazolidone, g/l	pH
0	Orange yellow	13.8	1.52	10.0
1/4	Orange red	——	1.46	——
1/2	Orange red	——	1.37	——
3/4	Orange red	——	1.24	——
1	Orange red	——	1.17	10.05
2	Orange red	——	0.70	——
4	Orange red	——	0.38	10.2
6	Orange red	——	0.15	——
7	Orange*	——	0	——

* Although all pyrazolidone has been transformed into hydroxypyrazole, the solution remains orange colored, contrary to Solution No. 2. The color must be ascribed to the oxidation products of hydroquinone disulfonate.

Solution No. 7

Time of oxidation, hours	Color	Hydroquinone, g/l	Hydroquinone disulfonate, g/l	1-Phenyl-3-pyrazolidone, g/l
0	Colorless	0.4	12.4	1.46
1/2	Colorless	——	——	1.46
1	Colorless	——	——	1.46
1 1/2	Pale yellow	——	——	1.44
2 1/2	Yellow	——	——	1.39
4 1/2	Orange red	——	——	0.74
8	Red	——	——	0.12

Solution No. 8

Time of oxidation, hours	Color	Hydroquinone monosulfonate, g/l	Hydroquinone disulfonate, g/l	1-Phenyl-3-pyrazolidone, g/l	1-Phenyl-3-hydroxypyrazole, g/l
0	Colorless	0.9	12.4	1.52	——
1/4	Pale yellow	——	——	1.49	——
1/2	Pale yellow	——	——	1.45	——
3/4	Orange yellow	——	——	1.37	——
1	Orange red	——	——	1.31	——
2	Red	——	——	1.08	0.22
4	Red	——	——	0.68	——
6	Red	——	——	0.25	——
7	Red	——	——	0.17	0.67

Solution No. 9

Time of oxidation, hours	Color	Hydroquinone monosulfonate, g/l	Hydroquinone disulfonate, g/l	1-Phenyl-3-pyrazolidone, g/l
0	Colorless	2.7	9.7	1.52
1/2	Pale yellow	——	——	1.49
1	Pale yellow	——	——	1.49
2	Pale yellow	——	——	1.41
3	Orange red	——	——	1.15
4	Red	——	——	0.82
5	Red	——	——	0.58
7	Red	——	——	0.21

Discussion

A mechanism for the regeneration of Metol in MQ developers has been proposed by G. I. P. Levenson.[5] If we accept the same mechanism for 1-phenyl-3-pyrazolidone, we can write the following reactions:

1-phenyl-3-pyrazolidone + O_2 → oxidized 1-phenyl-3-pyrazolidone (I)

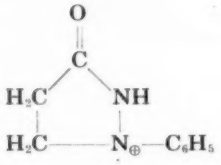
oxidized 1-phenyl-3-pyrazolidone + hydroquinone → 1-phenyl-3-pyrazolidone + quinone (II)

quinone + sodium sulfite → hydroquinone monosulfonate + sodium hydroxide (III)

Reaction II can be considered as a redox-equilibrium. This equilibrium will be shifted to the right, when the quinone is taken away, for instance by sodium sulfite.

Quantitative regeneration of 1-phenyl-3-pyrazolidone can only be expected in the presence of sufficient hydroquinone or hydroquinone monosulfonate in combination with sodium sulfite.

The structure of the oxidized form of 1-phenyl-3-pyrazolidone in Reaction I is unknown. Since 1-phenyl-3-hydroxypyrazole and hydroquinone in the presence of carbonate and sulfite do not give any regeneration, we must accept an intermediate oxidation step. A possible structure has been proposed by T. H. James:[6]



This form has an unpaired electron and will be unstable. In the presence of hydroquinone and sulfite it will be reduced. In the absence thereof it will be oxidized to hydroxypyrazole. So we can write:

1-phenyl-3-pyrazolidone $\xrightarrow{-e}$ semiquinone of pyrazolidone

semiquinone of pyrazolidone + hydroquinone ⇆ 1-phenyl-3-pyrazolidone + semiquinone of hydroquinone

semiquinone of hydroquinone ⇆ hydroquinone + quinone

quinone + sodium sulfite → hydroquinone monosulfonate + sodium hydroxide

5. G. I. P. Levenson, *Phot. J.*, **89B:** 18 (1949).
6. T. H. James, *PSA Jour.*, **19B:** 160 (1953).

An indication of an intermediate semiquinoide-form of the pyrazolidone[3] is given by the maximum in the absorption curve at 516 mμ of PQ developers which are strongly oxidized.

The tabulated results are in accordance with this mechanism. 1-Phenyl-3-pyrazolidone is regenerated in the Baths 4 and 5, where hydroquinone (or monosulfonate) is present in sufficient quantity in combination with sodium sulfite. Even in the Baths 7 and 8 where the quantities of hydroquinone or the monosulfonate are only one tenth of those in Baths 4 and 5, there is, at least at the start, some regeneration of the pyrazolidone. In the case of the monosulfonate, however, regeneration is less quantitative than in the case of hydroquinone.

When all monosulfonate has been transformed into disulfonate, the concentration of 1-phenyl-3-pyrazolidone rapidly decreases and hydroxypyrazole is formed. The color of the liquid changes from yellow through orange to red. The orange coloration is caused by oxidation of the disulfonate.

When there is an absence of sodium sulfite (Baths 1 and 3) or hydroquinone (hydroquinone monosulfonate) (Baths 2 and 6), hydroxypyrazole is immediately formed. However, the decrease of pyrazolidone in Bath 6, which contains hydroquinone disulfonate, is remarkably slower than the decrease in Bath 2, where the disulfonate has been omitted.

Analysis has shown that the transformation into hydroxypyrazole is quantitative only when sodium sulfite is absent. In the presence of 40 grams sulfite no more than 50 to 70% hydroxypyrazole is formed. An explanation of this fact has not yet been found.

In a preliminary investigation of the photographic properties of PQ developers, we have found that the super-additivity is also strongly dependent on the sodium sulfite concentration. It increases with growing concentrations. It remains nevertheless questionable, as pointed out by James,[6] whether the superadditivity can be explained by the regeneration theory. James has given an explanation on the basis of charge-barrier depression by oxidation products of 1-phenyl-3-pyrazolidone with a quaternary, positive-charged nitrogen atom. At this time, however, we do not see how the strong dependence of the superadditivity on the sodium sulfite concentration can be explained by the charge-barrier theory.

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Volume 4, Number 3, May-June 1960

The Effect of Film Thickness Variations on Coherent Light

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The introduction of commercial photographic film into the aperture of an optical system disturbs the phase relationship of the transmitted light. This disturbance is due to variations in thickness and refractive index present in the film. Such physical variations in film may be made visible, as contour lines, by obtaining light interference between the front and back film surfaces. Photographs of the interference pattern were measured and calculations of light-path variations made. A qualitative analysis showed that film-base thickness variation was primarily responsible for phase front deterioration. Measurements taken on a number of films showed only a few acceptable by Rayleigh limit standards. More films were found to be acceptable when immersed in a liquid whose index of refraction nearly equaled that of the film. A diagram is included to show how closely the film and liquid indices must match for any particular film quality to affect coherence, due to thickness, by no more than one Rayleigh limit. It is concluded that a special effort is necessary by photographic film manufacturers to provide satisfactory films, but that some improvement can be obtained by the use of a liquid gate.

Photographic film has been applied in a relatively new way in recent years, placing additional demands on the perfection of film manufacture. The film is used in the aperture of an optical system rather than, as is usual, in the image plane. Geometric patterns are photographed and this record, called a hologram, is placed in the optical aperture to control the phase of the transmitted light, thereby producing a desired effect in the image plane.[1-5] Unfortunately, variations in film thickness and refractive index affect the phase in random fashion, thus preventing the desired result. Under these conditions of use, variations in thickness, refractive index, and surface quality are of prime importance.

The effect of placing film with nonuniformities in an optical-system aperture is to disrupt orderly wavefronts, causing a diffusion of the light at the image points. This diffusion can take the form of a displacement due to an optical wedge in the film, a defocusing of the image due to the lens power of a spherical depression or projection on the film, or a combination of both. Higher-order effects are also present, due to saddle curves and inflection points.

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2. P. Kirkpatrick and H. M. A. El-Sum, *J. Opt. Soc. Am.*, **46:** 825 (1956).
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Experimental Procedures

A study of these variations in film was made possible by taking photographs of the pattern resulting from interference in monochromatic light occurring at normal incidence between light reflected from the front and back surfaces of the film. The apparatus (Fig. 1) consisted of a 100-w mercury arc lamp, a piece of flashed opal glass, a curved-object film holder (2-ft cylindrical radius), a 5461-A interference filter and a 4-by-5 view camera. The light source was made broad by using an opal glass after, but near, the lamp. This was necessary in order to obtain specular reflection into the lens from slightly irregular surfaces, such as curl or wrinkles in the film. The light source and camera lens were placed as close together as possible and approximately at the center of curvature of the film holder. In this way, the front and rear surfaces of the film formed a double cylindrical reflector which was tilted to focus the reflected light from the source into the photographic lens, thus filling the lens field with light. It was necessary to close the lens to approximately $f/45$ in order to get contrasty fringes, since wider openings allowed displacement of fringes with consequent smearing.

As a first test, interference pictures of a number of film samples were taken with the above apparatus and sorted into a distribution of visually discrete steps of average fringe concentration. From this

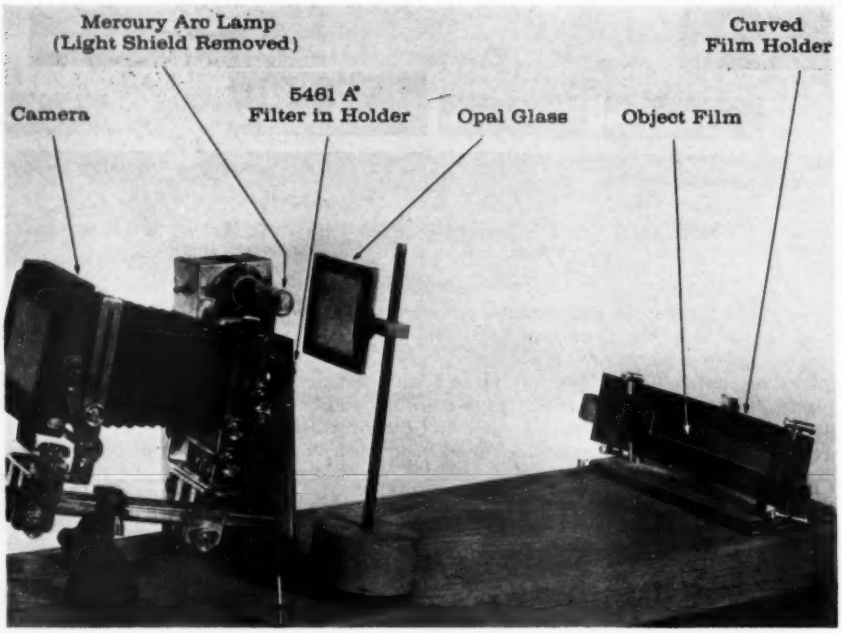

Fig. 1. Experimental apparatus for photographing interference pattern due to the reflection from the two surfaces of clear photographic film.

distribution, a quality chart (Fig. 2) was constructed with quality ratings ranging from A through H. A chart was also made of the distribution of a number of films from six different manufacturers, of which three manufacturers were domestic and three were foreign (Table I).

At this point two questions needed to be answered. They were: (a) whether the base or the emulsion was responsible for the optical variation; and then (b) whether the surface or the index was more responsible. To determine answers, second and third tests were performed.

The second test was made by photographing five different films, with and without emulsion, to show whether the film base or the emulsion played the more important part in producing high fringe concentrations. The test was begun by taking a 4-ft strip of unexposed film and developing and fixing it clear. The film was then cut into two pieces, each 2 ft long. The emulsion was then stripped from one piece, and both pieces were photographed, using the techniques and apparatus described above. It was evident that far more difference existed between

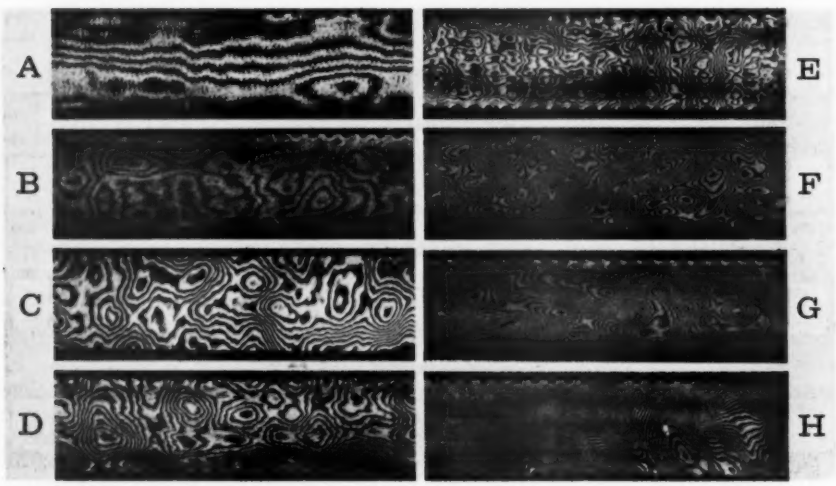

Fig. 2. Interference patterns due to optical path variation in light reflected from clear photographic film. Reading from A to H, samples are graded from least to most variation. Interference wavelength — 5461 A

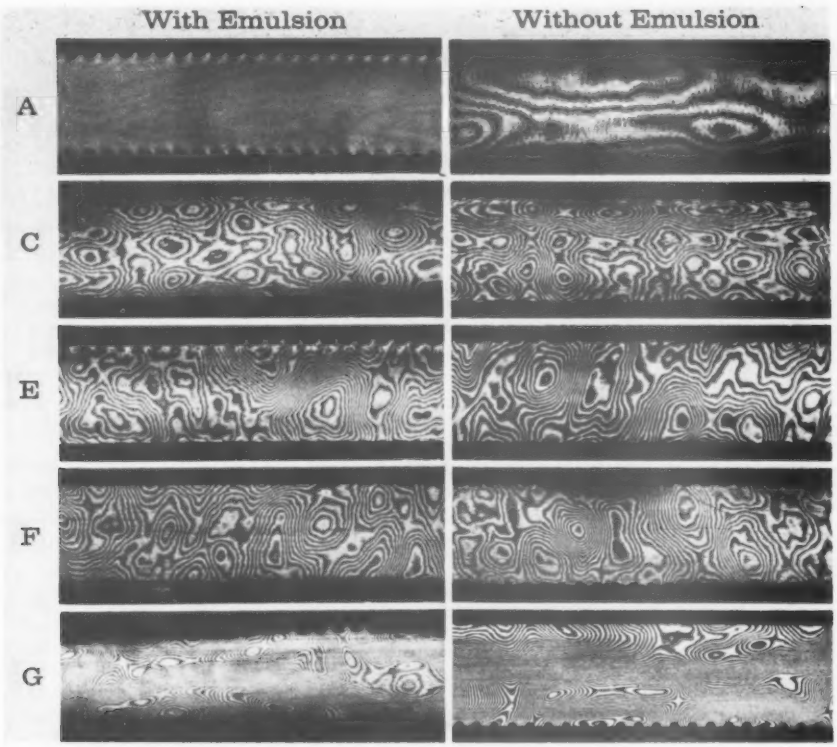

Fig. 3. Interference patterns showing the effect of emulsion on the optical path variation. Interference wavelength — 5461 A.

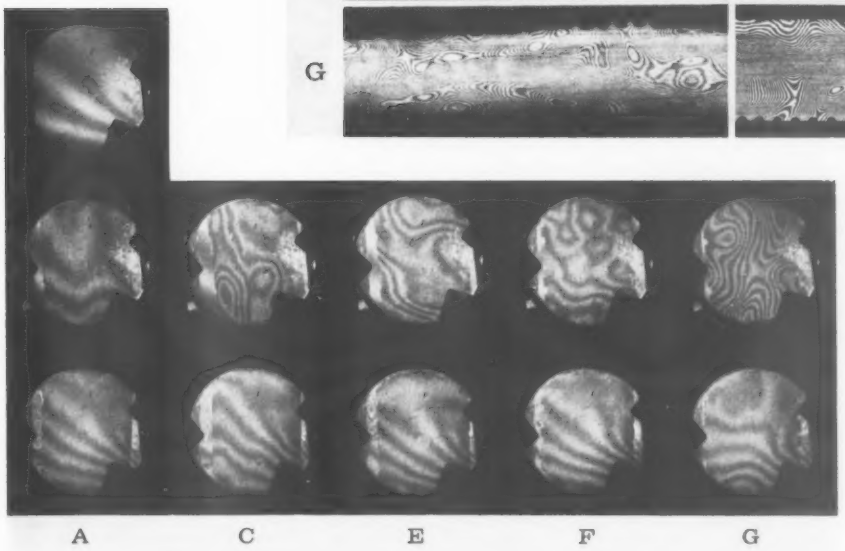

Fig. 4. Interference photographs made with liquid gate using the reflection from the nternal aluminized surfaces of a glass cell, showing surface vs index variation. Top, no film; middle row across, dry; bottom row across, wet.

films than between the same film with and without emulsion (Fig. 3).

The third test was performed to ascertain whether change of thickness or change of refractive index is more responsible for the variation in optical path length. The test consisted of obtaining light interference between the back and front planoglass surfaces of a cell and then noting the change in the interference pattern when film alone or film and a liquid of matching index were introduced into the cell (Fig. 4). The cell plates were half aluminized and adjusted nearly parallel so that very few fringes were present. The introduction of film altered the fringe pattern, but the addition of a liquid whose index of refraction matched that of the film brought the fringes back nearly to the original pattern. A liquid, called Refractasil, made by the General Electric Company, was used for this experiment. The same apparatus described above was used to photograph these fringes, except that the curved film holder was replaced by the liquid cell just described. Figure 4 shows the interference fringes for the cell alone with no film and for five samples of film with and without liquid. The fact that the wet film interference

TABLE I

Distribution of samples of film manufactured by various companies with respect to film-thickness variation, sectioned into arbitrary quality ratings.

Manufacturer	Quality A	B	C	D	E	F	G	H
1	x	xx	x					
2		xxxx	x	x	x	xx		xx
3			xx	x	xx	xxxx		
4				x		xx		
5					x	x	xx	
6						xx		

pictures look nearly like the picture of the cell with no film indicates that most of the optical path variation is due to the film surface variation and very little is due to variation of film refractive index. Film thickness thus appeared to be mainly responsible for the variation in optical path length.

It was noted that more fringes appear in the wet film than in the dry cell photographs. This is due to shorter effective wavelength in the liquid. Also, the fringe count in the case of dry film is one-third that which appears in interference between the front and back surfaces of the film of the first test.

Discussion of Results

Quantitative measurements were obtained by counting fringes linearly over a measured distance on the film-surface-interference photographs. This permitted quantitative representations of the light deviation due to wedge for the various quality ratings. Two values were obtained, one for average deviation and one for maximum deviation. The average deviation was obtained by counting fringes linearly over the interference photograph and dividing the number of fringes by the distance covered in millimeters. A computation was then necessary to express this as average deviation. Maximum deviation was obtained by obtaining the fringe count divided by distance for a small length at the position where the fringe system was the finest.

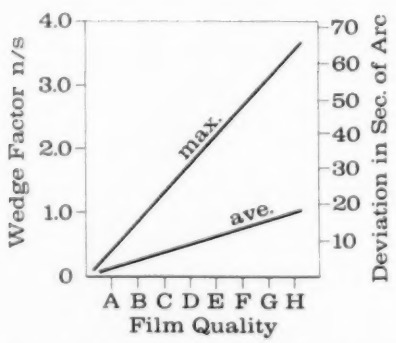

Fig. 5. Average and maximum deviation due to light transmission through photographic films having various levels of film thickness variation.

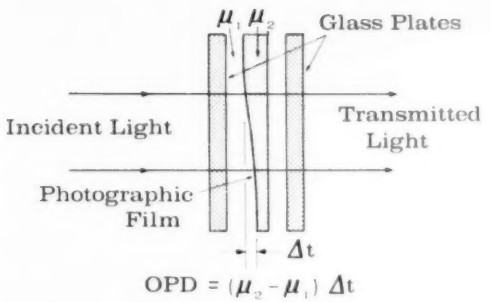

Fig. 6. Transmission optical path difference: Case A, liquid gate. The diagram illustrates the effect of film thickness variation and immersion liquid index on optical path length of light passing through a liquid cell.

The formulation used was:

$$D = \frac{(\mu - 1)\lambda}{2\mu} \cdot \frac{n}{S}$$

where D = deviation angle
μ = refractive index (1.478)
λ = wavelength of light (0.0005461 mm)
n = fringe count
S = distance over which fringes were counted

Figure 5 shows the average results obtained, using eleven different photographs.

Since the optical path variation defect was found to be principally due to variation in base thickness, the pattern of fringes obtained in the photographs of Fig. 2 are essentially a topographical map of the optical thickness variation in the film. The space from one dark line to another shows a thickness change represented by:

$$\begin{aligned} \Delta t = \lambda/2\mu &= 0.0005461/(2 \times 1.478) \\ &= 0.00018 \text{ mm/fringe} \\ &= 0.0000073 \text{ in./fringe} \end{aligned}$$

where Δt = thickness change. Maximum thickness variations can be obtained by counting fringes and multiplying by the above thickness change per fringe. On this topographical map:

1. Parallel lines indicate a slope forming an optical wedge. The finer the line structure, the steeper is the slope.
2. Concentric circles indicate either hills or depressions.
3. Saddle points usually separate two hills in one direction and two depressions in the 90° direction.
4. A hill and a depression are separated by more or less parallel fringes, where the finest line structure occurs at the inflection point.

In order to determine the effect of film-thickness

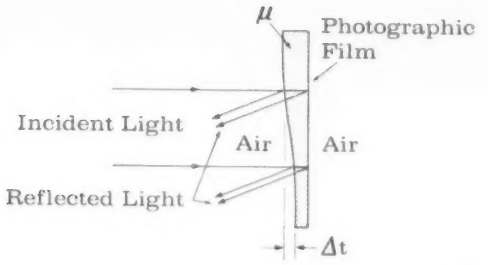

Fig. 7. Interference in photographic film: Case B. The diagram illustrates the effect of film thickness variation on optical path length of light reflected from its two surfaces.

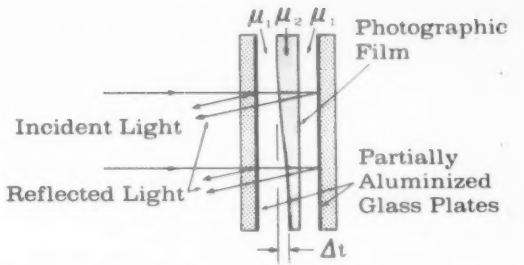

Fig. 8. Interference in liquid cell: Case C. The diagram illustrates the effect of film thickness variation and immersion liquid on optical path length of light reflected from the two internal surfaces of a liquid cell.

variation during use or measurement, three separate situations must be considered:

Case A: Transmission of light through film

Case B: Light reflected from both surfaces of film

Case C: Light reflected from two glass plates having film, film and liquid, or no film between them

Since these three cases are slightly different mathematically, they are treated separately.

Case A (Fig. 6)

In this situation, film is in use in a gate which may or may not contain a liquid. It is assumed that light passes through thicker and thinner portions of the film and the optical path difference (OPD) is given by the formula

$$\text{OPD} = (\mu_2 - \mu_1)\Delta t.$$

Case B (Fig. 7)

This is the case where interference takes place between light reflected normally from the front and back surfaces of a piece of film. In this case, black lines appear where a path difference between the front and back reflections is a whole number of wavelengths. The formula for change of thickness is

$$\Delta t = n\lambda/2\mu,$$

where n is the number of black (or white) lines counted between points. This applies to the pictures in Figs. 2 and 3.

Case C (Fig. 8)

In this case, interference occurs due to combining light reflected from the partial mirror surfaces of the two glass plates. One of the reflected rays will have traveled twice through the film and its immersion medium. The formula for optical path difference is

$$\text{OPD} = 2(\mu_2 - \mu_1)\Delta t,$$

and for the number of fringes associated with a change of thickness,

$$\Delta t = n\lambda/2(\mu_2 - \mu_1).$$

For these cases, certain deductions follow. First, upon comparing Case B with Case C (dry cell) it appears that the number of fringes will be different for the same change of film thickness. For

Case B, $n_B = 2\mu\Delta t/\lambda$; for
Case C, $n_C = 2(\mu - 1)\Delta t/\lambda$; and
therefore, $n_B = n_C\mu/(\mu - 1)$.

This shows that, for $\mu = 1.478$, the number of fringes for Case B is approximately three times the number of fringes for Case C. For this reason there are fewer fringes apparent in the Fig. 4 "dry cell" than in Fig. 3, although the same films were used. Secondly, upon comparing the "wet" cell with the "no film" cell it is noted that more fringes are apparent in the wet-cell case. This is to be expected, since the effective wavelength in the cell is λ/μ_2, which is smaller than the wavelength λ for the same cell in air. This means that we should find nearly 50% more fringes in the wet-cell case due to this effect.

Permissible Limits

In order to select a film having acceptable variations, the Rayleigh limit may be employed. This specifies that no more than one-quarter of the wavelength of light of optical path difference is permissible over the active aperture. OPD due to thickness variation (Δt) of a film (of index μ_2) immersed in a medium (of index μ_1) can be represented by the formula:

$$\text{OPD} = (\mu_2 - \mu_1)\Delta t$$

(Fig. 6). If the Rayleigh limit of a quarter of a wavelength ($\lambda/4$) is used as the maximum allowable departure from coherence, the formula for the maximum allowable thickness variation of the film becomes

$$\Delta t_{\max} = \lambda/4(\mu_2 - \mu_1)$$

For film immersed in air and using a green mercury lamp for monochromatic light, the permissible variation in film thickness is approximately 0.0001 mm, a very small variation indeed.

However, film may be immersed in a liquid whose index approximates that of the film.[6] A plot of the Rayleigh allowable film-thickness variation vs immersion liquid index for a film index of 1.478 is

6. J. G. Stott, G. E. Cummins, and H. E. Breton, *Jour. SMPTE*, **66:** 607 (1957); J. R. Turner, D. E. Grant, and H. E. Breton, *ibid.*, **66:** 612 (1957); D. A. Delwiche, J. D. Clifford, and W. R. Weller, *ibid*, **67:** 678 (1958).

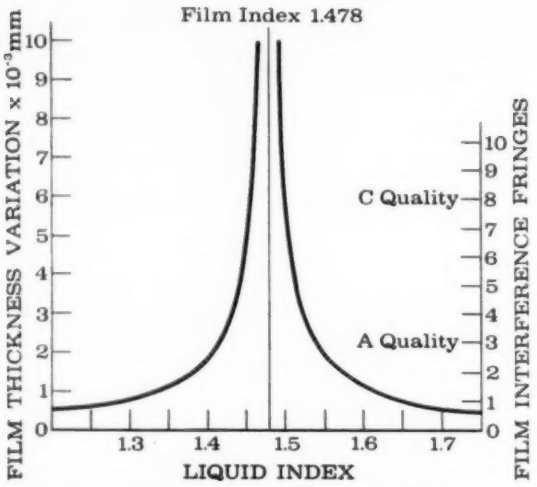

Fig. 9. Index-matching diagram, showing the film thickness variation that is permissible while remaining within the Rayleigh limit of one-quarter wavelength of optical path difference, using immersion liquids of various refractive indexes.

given in Fig. 9. The ordinate is also given in terms of a number of fringes as counted on an interference photograph of film thickness variation. (Film thickness per fringe is $t/n = \lambda/2\mu$.)

By counting fringes on the quality chart (Fig. 2), it will be seen that C quality has a maximum of about nine fringes from hill to depression, allowing an immersion liquid index variation from about 1.46 to 1.50. For film in air, a variation of only a half fringe can be tolerated. For film immersed in water ($\mu = 1.33$), variation of less than one and a half fringes can be tolerated.

An additional advantage is gained by the use of a liquid gate. Scratches and rough surface present on the film give rise to scattered light. The scattered light from films used in the optical aperture produce loss of contrast in the final image. The use of liquid in a liquid gate fills in the scratches and rough surface, thereby eliminating scattered light from this source.

When an immersion liquid is used, change of phase due to a relief image is eliminated. This phasing under some conditions may be in such a direction as to increase the illumination in the final image. If this happens, the liquid serves to reduce illumination, and its use is then classed as a disadvantage.

Conclusions

Through the use of light-interference measurements, it is concluded that change in film-base thickness is found to be the principal cause of variations of optical path length through film. For optical path-length variation, the film samples tested are distributed over a considerable range. A high degree of excellence in manufacture is necessary if film is to be used in an air aperture and coherence of light within the Rayleigh limit is to be maintained. The use of a liquid gate with film has both advantages and disadvantages. The advantages are:

(a) Reduced light-phase variation due to thickness variation
(b) Ease of retaining film in a plane by a glass plate cell
(c) Reduction of noise due to scratches and rough surface

The disadvantages are:

(a) Difficulties of handling liquid
(b) Elimination of phasing due to relief images

Some lack of match between liquid and film may be allowed without exceeding the Rayleigh limit for a particular film.

Statistically, it is evident that the sampling is inadequately small to prove any trend conclusively. Enough evidence is available, however, to indicate the advisability of pursuing this study further, and to reveal the advantage of expending efforts to achieve a substantial improvement in film quality.

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A High-Speed Color Printer

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A high-speed printer for making color paper prints from color photographic negatives has been engineered and constructed by Technicolor Corporation. Salient features of the printer are: automatic operation, two printing beams, high production rate, precoding of negatives, and stable operation. Customer negatives, size 120, are spliced into 500-foot rolls and transported automatically to eliminate the operator. Two negative rolls are handled simultaneously and in synchronism, exposing onto 7-in. wide color print paper. Printer capacity is about 5000 prints per hour for first prints from new negatives. Exposure time is 0.5 sec and cycle time is 1.2 sec per pair of negatives in the two printing beams. Prior to loading negatives into the printer, a precoding machine records a frame index mark plus density and color correction data on the margin of each negative. Precoding includes automatic discrimination between daylight and flash exposures. The 3-sigma limits for log exposure are ± 0.012; 3-sigma limits for negative transport are $\pm 1/64$-in.

Design features to attain fast, stable operation include: (*a*) 1000-w fixed-intensity printing lamp to eliminate color temperature variations; (*b*) Dichroic division and recombination of white light between lamp and negative gate to allow fast, independent mechanical control of red, green, and blue light components, each over 100:1 intensity range to accommodate negatives from four stops underexposed to five stops overexposed; (*c*) Fixed exposure time (0.5 sec) for all negatives to eliminate possible trouble due to reciprocity failure in the color print paper; (*d*) 420-cycles/sec chopped null balance for red, green, and blue monitor end-on multiplier phototubes, to eliminate printer drift due to phototube and amplifier instability; (*e*) Null balance photometric control of undercorrection for negative density.

In the early part of 1957, the design and fabrication of a high-speed printer for making color prints from Kodacolor negatives was begun. The printer is now completed and is in successful operation with a capacity of 5000 prints/hour.

Originally, several possible systems of exposure control were considered but rejected because of specific disadvantages which, in the opinion of the authors, outweighed their advantages.

One possible system involves constant illumination at the negative plane with variable time as the control. This has the following disadvantages:

(1) Differential reciprocity law failure among the layers in the color print paper requires electronic or electrical means for compensation, leading to added capital cost, maintenance, and system instability.

(2) Inaccuracy is caused by extremely short exposure time required for underexposed negatives.

(3) Production is slowed down when overexposed negatives are printed.

Another possible system involves the control principle of quasi-constant intensity at the paper plane. The lamp intensity is caused to vary with negative density but because of thermal lag, the integrated negative transmission control compensates by varying the exposure time. The disadvantages of this system are: (1) variable color temperature; and (2) some reciprocity law failure requiring electrical or electronic means for compensation.

A third system which can be used utilizes the principle of constant exposure time with variable lamp intensity. This eliminates reciprocity law failure but retains variable color temperature and slows down production capacity to allow for thermal lag.

All of the systems listed above require the red, green, and blue components to be printed in succession, which limits printer production capacity.

Another control principle which can be used depends upon constant light intensity at the negative plane, starting the exposure period with white light, and cutting off the red, green, and blue exposures at the proper time by insertion of minus red, minus green, and minus blue filters, respectively. This system, while increasing production capacity, still involves the following disadvantages: (1) reciprocity law failure, with attendant capital and maintenance costs and drift of electrical compensation devices; and (2) production slow-down when printing overexposed negatives.

Systems can be designed which depend, for constancy and reproducibility, on the stability of electronic circuitry and of absolute sensitivity of photo-

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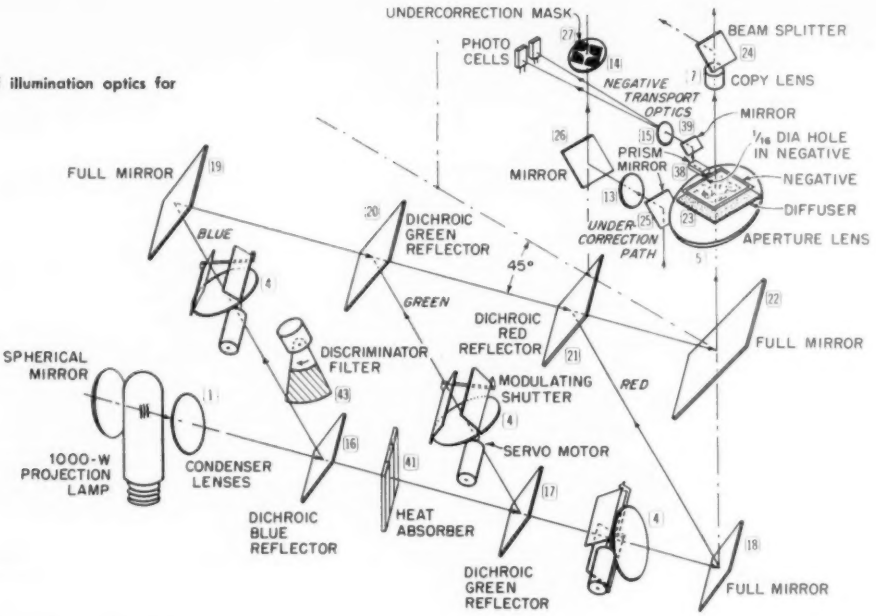

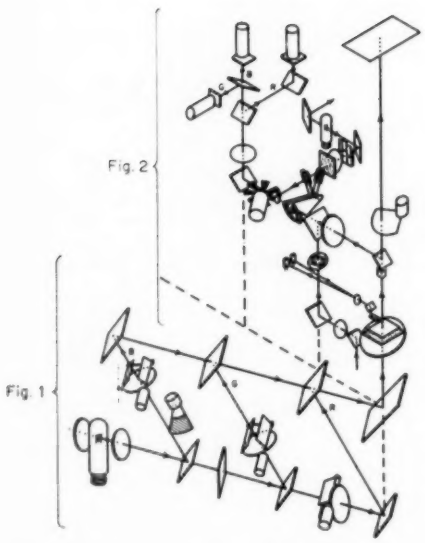

Schematic diagram of entire optical system for one of the two printing paths, showing the relationship between Figs. 1 and 2.

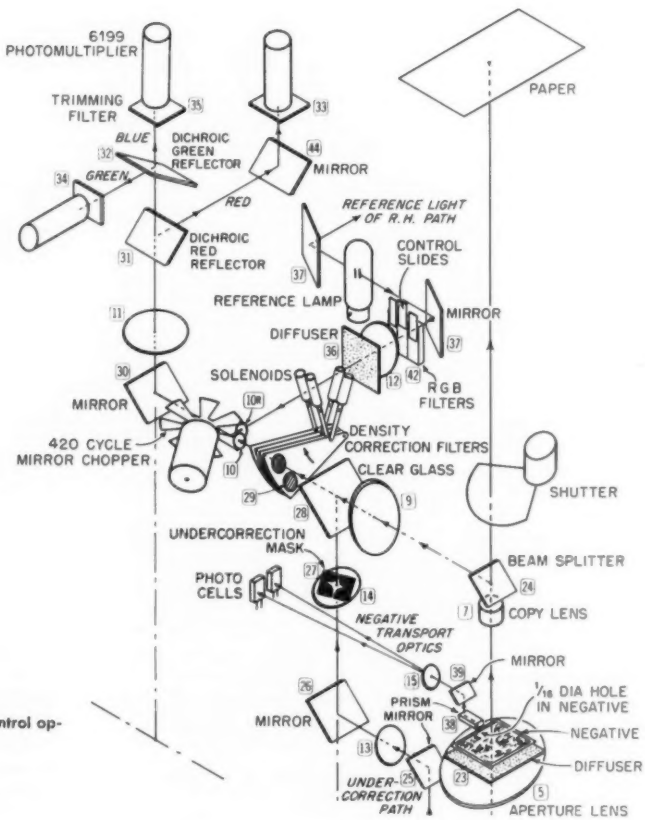

Fig. 2. Schematic diagram of exposure control optics for one printing path.

sensitive devices. This is true not only of the exposure control, but also of undercorrection and density and color subject failure corrections.[1]

In addition, it is usual to design printers requiring the constant attendance of an operator who feeds strips or single customer negatives into the printer, encoding each frame for density or color subject failure correction at the same time.

In order to eliminate most of the disadvantages inherent in the above systems, the new printer was designed and constructed with the following salient features:

(1) The printer is completely automatic, has a capacity of 5000 prints/hour, and requires no operator.

(2) Lamp intensity and, therefore, color temperature are maintained constant.

(3) Exposure time is maintained constant, thereby eliminating reciprocity law failure and electronic devices for compensation.

(4) The integrated negative transmission control is a completely null system, independent of electronic or photosensitive drift and dependent only on the constancy of emission of a voltage-regulated reference lamp.

(5) Undercorrection[1,2] is applied photometrically, retaining the null control feature.

(6) Density subject failure corrections[1] are applied photometrically, again retaining the reliability of the null system.

(7) Customers' negative strips are spliced into 500-ft rolls. These rolls are then fed through separate encoding machines where operators frame the pictures for printing by punching a $\frac{1}{16}$-in. diameter control hole in one edge of the negative and one or more of a series of $\frac{1}{32}$-in. diameter holes in the opposite edge for density and/or color subject failure correction.

(8) The printer has two complete printing paths in order to utilize a single strip of 7-in. wide paper.

(9) In each path, the negative is automatically advanced rapidly and framed accurately by means of the control hole (see (7)) which actuates, photoelectrically, a clutch-brake drive.

(10) Insertion of density and color subject failure correction is accomplished electro-pneumatically, by means of the precoded holes (see (7)), utilizing the binary system.

(11) Two rows of prints are made through offset negative and positive apertures onto 7-in. wide Kodacolor paper, using a paper transport of conventional design.

The only departure from a true null system is in the matter of color subject failure correction. Since these correction increments are small in comparison with density corrections and since operators cannot accurately judge the increment of color correction to apply, it is believed that extreme stability is not required. Color correction, therefore, is applied electronically and is reliant for accuracy on the stability of electronic and photosensitive devices.

Description of Printer and Its Functions

Illumination Optics

Figures 1 and 2 show schematic diagrams of the optical system for one of the two printing paths.

Light from a 1000-w projection lamp, Fig. 1, is reflected by dichroic mirrors 16 and 17 and the full mirror 18, to produce blue, green, and red light paths, respectively. Filament images are formed in the three relay lenses 4. The blue, green, and red components are recombined by reflection from the full mirror 19 and dichroic mirrors 20 and 21, respectively. Superimposed blue, green, and red images of the condenser lens 1 are formed at the aperture lens 5 by the relay lenses 4. Between the aperture lens 5 and the negative plane is a diffusion plate which minimizes the printing of negative surface scratches.

Since the relay lenses 4 are at nodal planes of the optical system, modulator shutters are placed at these positions. A simple mechanical linkage causes both blades on each modulator to open or close together when the shaft of one shutter is rotated by a servomotor.

When the shutters are wide open, the exposed illuminated area of the relay lenses is 3 by 3 in.; when closed, 3 by 0.030 in. The exposure range of the printer, therefore, has a ratio of 100:1 or a log E difference of 2.00. The exposure range required for a series of negative exposures ranging from four camera lens stops underexposed to four stops overexposed, a total of nine stops, has been empirically found to be 50:1 or a log E difference of 1.70. Beyond this range, prints become unacceptable from a quality standpoint, although the customer may insist he wants prints anyway.

Figure 3 shows a plot of log area (log E) between shutter blades vs. angular rotation in degrees of servomotor shaft for these modulators. Because of the cosine effect, a rotational error in terms of log E does not vary to a marked degree over the entire range of shutter position.

Whereas, normally, shutter images would be formed at copy lens 7, Fig. 1, producing variable area modulation, the diffuser between aperture lens 5 and the negative destroys any shutter image at the copy lens and thereby produces a variable intensity modulation.

Integrated Transmitted Energy Control System

Immediately adjacent to the copy lens 7, Fig. 2, in the optical path of the image space, is a beam splitter 24, consisting of a thin glass optical flat set at 45° to the optical axis. This serves to divert (reflect) approximately 8% of the light intended for the paper plane.

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2. C. J. Bartleson and R. W. Huboi, *Jour. SMPTE*, **65:** 205 (1956).

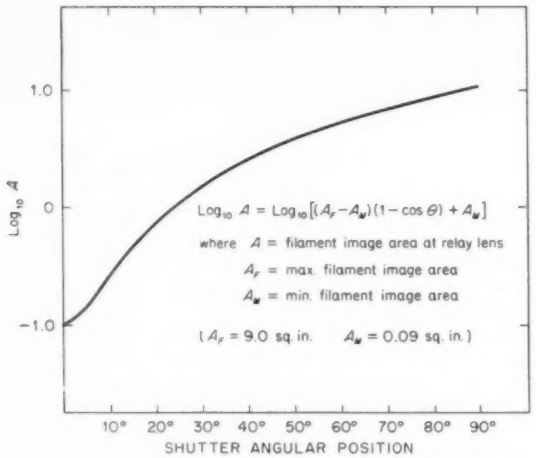
1.0
0
−1.0
Log10 A
Log10 A = Log10[(Ar−Aw)(1−cos θ) + Aw]
where A = filament image area at relay lens
Ar = max. filament image area
Aw = min. filament image area
(Ar = 9.0 sq. in. Aw = 0.09 sq. in.)
10° 20° 30° 40° 50° 60° 70° 80° 90°
SHUTTER ANGULAR POSITION

Fig. 3. Curve showing relationship of area between modulator shutter blades and angular position of servomotor shaft.

By means of lens system 9, an image of copy lens 7 diaphragm is formed in the small lens 10 which, in turn, is imaged by lens 11 at the photocathode surfaces of three head-on photomultiplier tubes after separation once again into blue, green, and red components by the two dichroic mirrors 31 and 32. In front of the photocathode surfaces are absorption-type trimming filters 33, 34, and 35.

The quantity of blue, green, and red energy reaching the respective photocathodes is always a fixed fraction of the integrated blue, green, and red energy, respectively, reaching the paper plane.

The reference lamp, Fig. 2, is a concentrated filament lamp operated at approximately one-third rated voltage in order to achieve long life and high stability. Beyond this lamp and in the order of appearance, is a block of glass (42) composed of adjacent strips of a blue, green, and red absorption filter whose spectral transmission bands match closely the sensitivities of the blue, green, and red sensitive layers, respectively, of the paper emulsion, a lens 12, and a diffusing medium. Thus, the small lens 10R is uniformly illuminated by a mixture of blue, green, and red reference light.

In the light path, and at an angle of 45° to the optic axes of lenses 10 and 10R, is a 7-bladed reflective chopper disk driven by a 60-cycle synchronous motor. The chopper rotates at 60 rps and produces, alternately, images of lenses 10 and 10R at the photocathode surfaces at the rate of 840 alternations or 420 cycles/sec. The energy reaching each photocathode, therefore, from lens 10 is constantly being compared to that from lens 10R. If the energies from lenses 10 and 10R striking a photocathode surface are unbalanced, there is a succession of direct-current pulses of alternating unequal amplitudes. This signal is amplified to a useful level. This amplified voltage is then fed to the control winding of the corresponding modulator servomotor.

External to the printer is a motor generator set which supplies 420-cycle, 110-v power to the reference windings of the servomotors. The motor of this set is powered from the same 60-cycle power source as the synchronous chopper motor. The two, therefore, are locked in synchronism.

The control voltages from the modulator amplifiers to the control windings of the servomotors are phased so as to be in quadrature with the reference voltage from the 420-cycle generator. Thus, if the energies arriving at a photocathode from lenses 10 and 10R are unbalanced, the corresponding servomotor shaft will rotate in a direction so as to balance the two energies.

Shutter movement and the balance position are independent of photocathode sensitivity drift or amplifier gain drift within reasonable limits. If there should be a large decrease in photocathode sensitivity or amplifier gain, driving torque on the servomotor shaft would be materially reduced, increasing shutter response time and decreasing the accuracy of approach to a balance position, but this behavior would be in the nature of equipment breakdown calling for repair, rather than in the nature of ordinary operational drift.

Actual tests have shown that within the limits of maximum to one-third maximum amplifier gain, there is no measurable change in modulator response time or accuracy of shutter position at the null point.

Complete faith has been placed in the reliability of the reference lamp. Since this lamp is operated at one-third its rated voltage from a step-down regulating transformer, long life free from short-term drift is assured.

Continuous tests over periods of from three to four days duration have shown, after statistical analyses, that if the reference lamp is allowed an initial warm-up period of one-half hour, the 3σ value of the control system is, in log E terms, ± 0.012. Except for the reference lamp, all functions can be utilized immediately from start-up, that is, cold, without any effect on accuracy of control.

With reference to the three (R,G,B) absorption filter strips 42 in the reference light path, Fig. 2, the exposure control can be varied at will at this location. This is accomplished by means of a metal strip slide in front of each filter. Each slide is attached to a micrometer head. An opening, whose width is a logarithmic function of the height, is cut in the slide. As the slide is moved up or down by turning the micrometer screw, the exposed area of the filter varies logarithmically as the slide moves linearly. In this manner, equal angles of rotation of the micrometer screw produce equal log I increments of reference light reaching the photocathode of a photomultiplier through the particular filter involved. Thus, the printing light for the same component will be changed by the same log I increment, because the modulator shutter will be forced to open or close to the extent that the light

from lens 10 will once again match that from lens 10R.

The dowser shutter which controls the exposure time of the printer is shown schematically in Fig. 2, just beyond the beam splitter 24. Because of this arrangement, at no time is either the reference light or the printing light cut off from the control system. This affords the modulators the opportunity of arriving at their correct printing positions as the negative frame is transported into printing position. By the time the negative aperture is closed, the modulator shutters are usually in printing position.

After the dowser shutter has been caused to open, it is held in that position by means of an adjustable electronic timer. Exposure time for the printer has been established at 0.50 sec. The accuracy of the electronic timer has been determined to be ± 0.01 sec.

Since the printer in its final form is capable of producing 5000 prints/hour, any malfunction of the modulators would become very costly. For example, if one of the modulator shutters were to become jammed or were to fail from some other cause, thousands of worthless prints could be turned out before this failure could be discovered. To avoid this, an electronic error signal detector was designed and incorporated. Its function is to prevent the dowser shutters from opening until the residual error signals from all six modulators in the printer have been reduced to a predetermined amplitude.

Density Subject Failure Corrections

It is frequently desirable to alter the integrated transmitted energy control of a printer so that the density of the print made from a negative having density subject failure can be made greater or less than would be the case if the control system were to function normally.[1]

Toward this end, an assembly of four semaphore blades operated by solenoids has been placed in the picture control path, Fig. 2, between lenses 9 and 10. Each blade carries a neutral density filter. The filter densities are based on a quasi-binary system. The density values are 0.075, 0.150, 0.300, and 0.375. For normal printing, the filter whose density is 0.375 remains in the light path.

By interposing various combinations of these four filters in the light path, the normal log E of the blue, green, and red printing light can be changed in a negative direction in five steps, and in a positive direction in six steps. Each step produces an incremental log E shift of 0.075. This type of correction does not alter the null principle of the control system. Since there is no infrared radiation and very little visible radiation in this path, gelatin filters can be used without fear of crinkle or fading.

The density correction filters are operated by pneumatic sensing of the negative coding holes.

In the under surface of the front edge of each negative gate is a row of $\frac{5}{64}$-in. diameter holes (Fig. 4). Low-pressure air is fed constantly to these holes. Just below, in the aperture plates, are corresponding holes which are in juxtaposition when the gates close. Air cannot enter the latter holes when covered by the negative. If, however, one or more $\frac{1}{32}$-in. holes have been punched into the negative by the encoding operation, air then is fed through the corresponding aperture plate hole or holes to pneumatic switches (Fig. 5) which cause the corresponding semaphores in the picture control path to be lifted. Thus, density subject failure correction is accomplished.

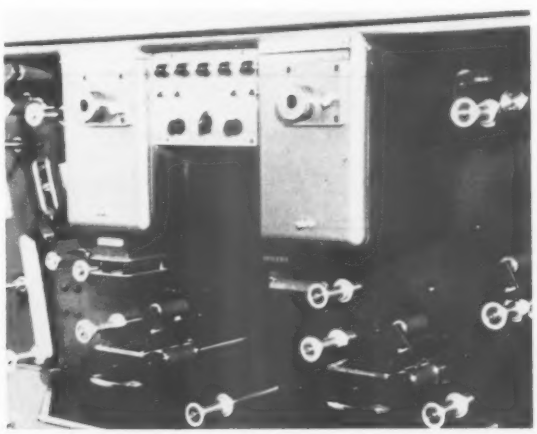

Fig. 4. Close-up view of negative apertures. Holes for feeding air to pneumatic switches can be seen in forward edges of aperture plates. Rubber-covered negative drive rollers are shown.

Fig. 5. Close-up view of retractable panel upon which are mounted pneumatic switches for actuating subject failure corrections, etc.

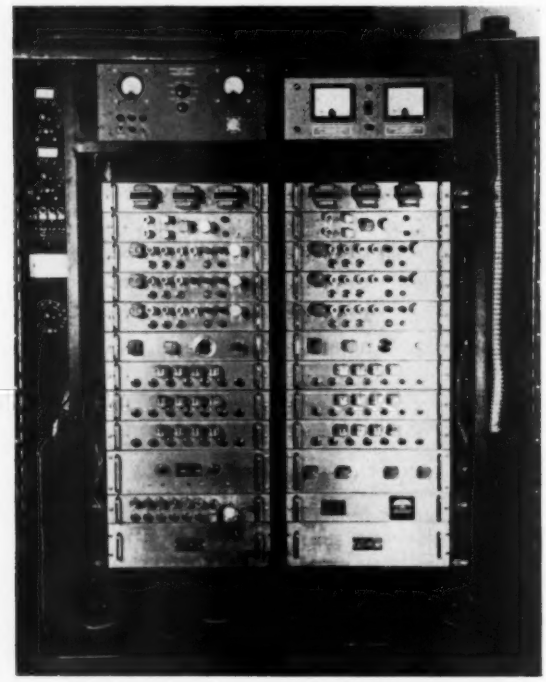

Fig. 6. Rear view of printer with back doors open, showing power supplies (top) and electronic chassis mounted on swinging doors.

Color Subject Failure Correction

Again, because some negatives display the phenomenon of color subject failure,[1] it is desirable, at times, to alter the integrated transmitted energy control of one, two, or even three of the color components.

Toward this end, there are nine pneumatic switches (Fig. 5), nine holes in both the negative aperture and the gate (Fig. 4), and nine punches on the encoder. These holes are in line with the density correction holes on the same edge of the negative. The nine holes are divided into three groups of three holes each. Each group controls one color component.

The three holes for each component permit, in a binary system, eight steps of correction in a minus direction. Each step produces an incremental log E change of -0.04. This is accomplished by tapping off a small amount of power from the 420-cycle reference voltage generator, phasing it by means of a resolver and combining it with the control signal voltage.

The amount of correction voltage to be mixed with the error signal for each step is controlled by seven pre-set potentiometers, each of which can be switched into the circuit by means of a matrix of three multiple pole relays (one for each hole). Each modulator amplifier chassis (Fig. 6), of which there are six (blue, green, and red for each printing path), has, therefore, in association with it, a color correction chassis containing seven potentiometers and three relays.

Undercorrection

The theory of undercorrection is fully discussed in the literature.[1,2] In summary, however, it can be stated that instead of keeping the integrated energy of the blue, green, and red components reaching the paper area at a constant value, regardless of the negative transmittance as exemplified by Curve (a) of Fig. 7, where $\log_{10}$ of the integrated energy at paper plane is plotted vs $\log_{10}$ 1/(integrated negative transmittance), it is better to have the printer control system create a response, as exemplified by Curve (b) of the same figure. This curve shows the $\log_{10}$ of the integrated energy at paper plane, as a linear function of $\log_{10}$ 1/(integrated negative transmittance) with a negative slope. Hereinafter, for convenience, $\log_{10}$ of integrated energy at paper plane, and $\log_{10}$ 1/(integrated negative transmittance) will be designated by log E and D, respectively. In other words, as D of each component changes, the control system of the printer does not fully compensate. When it comes to producing acceptable color prints from borderline subject-failure negatives, both density-wise and color-wise, without deliberate compensation as described in the two subsections immediately preceding this one, undercorrection accomplishes distinct and remarkably good results.

Experience has shown that if the slope of Curve (b) in Fig. 7 is maintained at approximately -0.10, for each component, optimum results are obtained.

With the exception of the subject printer, it is believed that undercorrection has been accomplished on all printers by electronic means. Once again, it was hoped that reliance on the constancy of electronic devices could be avoided.

As a result, a photometric means was devised which is completely effective and does not interfere with the null system of control.

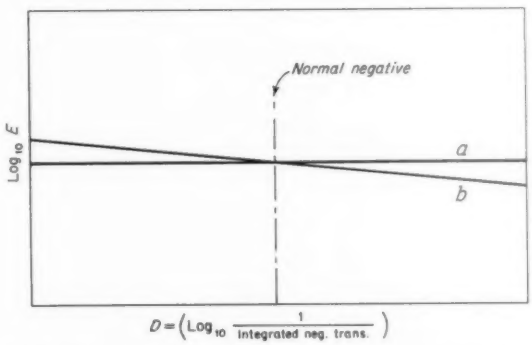

Fig. 7. Curve a — Log integrated energy at paper plane vs log inverse of integrated negative transmittance when printer exposure control functions normally; Curve b — Same plot as Curve a but with undercorrection fed into exposure control system.

The images of consenser lens 1 (Fig. 1) are focused by the three relay lenses 4 at the aperture lens 5. The focal lengths and the conjugate distances of lenses 4 are such that the images of the condenser lens 1 are considerably larger than the aperture lens 5. In addition, lens 5 is square-cut, which increases the overlap still more.

A full mirror (25) (Fig. 2) is placed at the overlap area of the condenser lens image to divert light into lens 13. The light, after passing through lens 13, is diverted by another full mirror (26) into lens 14.

Lens 13 serves a two-fold purpose. It forms a virtual image of the edge of condenser lens 1 between it and mirror 25, and it forms well-defined images of the three modulator shutter gaps at lens 14, since there is no diffusion in this path.

The light, after passing through lens 14, is diverted by the clear glass beamsplitter 28 into lens 10 and is added to the light coming from lens 9. Lens 14 serves to focus the virtual image behind lens 13 of condenser lens 1 at lens 10. The effect of varying the width of the modulator shutter gaps is to produce a variable area effect at lens 14, but a variable intensity effect at lens 10.

Thus, as the modulator shutters are forced open by the control system to compensate for a more dense negative, more energy is admitted to the photocathodes of the photomultiplier through the undercorrection path, with the result that the modulator shutters are not permitted to open as wide as would be the case if the undercorrection path were nonexistent.

If a thinner (less dense) negative comes into view of the negative aperture, the converse takes effect — that is, the shutters open a little more than would normally be the case. This produces an undercorrection effect at the paper plane.

It can be shown mathematically that if the undercorrection path is arranged as just described, a nonlinear relationship would exist between log E (at paper plane) and D. It can be shown that the relationship can be expressed by:

$$\text{Log } P = a - D - \text{Log } (b10^{-D} + C) \qquad (1)$$

where P denotes radiant flux at paper plane, D is defined above, and a, b and c are constants.

By differentiation,

$$\frac{d \text{ Log } P}{d D} = \frac{m10^{-D} - C}{b10^{-D} + C} \qquad (2)$$

where m = a constant.

Equation 2 states that the undercorrection value is not constant, since the slope of the log P vs D curve is a function of D.

If, however, an opaque mask is placed over lens 14, with a cut-out clear area whose shape is such that the transmitted energy is a nonlinear function of modulator shutter gap, the log P can be made to have a linear relationship to D, and the slope of the Log E at paper plane vs D curve can be maintained constant at some predetermined value.

The shape of the mask required to produce this linear relationship can be expressed by the following equation:

$$W = K \frac{\gamma}{\gamma + 1} h^{-\frac{1}{\gamma + 1}}$$

where W = width of mask opening (transverse to modulator shutter gap)

h = height of mask opening illuminated by shutter gap image

γ = desired slope constant of log E vs D curve

and K = a constant whose value is partly dependent on ratio of energy transmitted by beam splitter 28 to energy reflected by it.

Figure 8 shows the mask shape for $\gamma = -0.10$. In order to produce the required ratio of energy

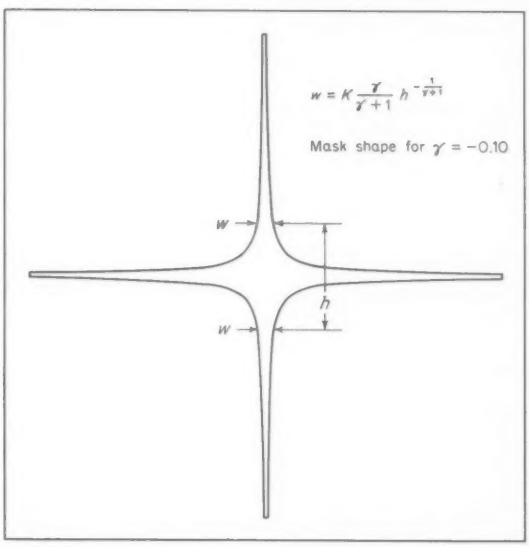

Fig. 8. Undercorrection mask required to be placed over Lens 14, Fig. 2, to produce Curve b of Fig. 7.

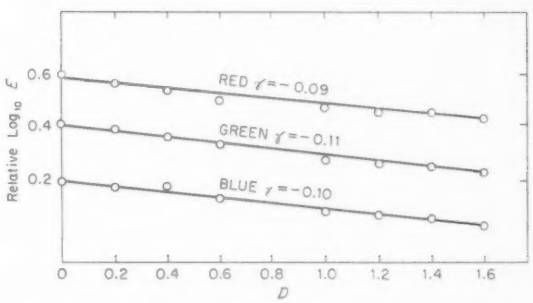

Fig. 9. Actual undercorrection curves of one printing path when mask of Fig. 8 is placed in undercorrection path.

transmitted to energy reflected by beam splitter 28 for the blue, green, and red components, a pack of CCY, CCM, and CCC filters is placed in the undercorrection path adjacent to lens 14. The value of the filters are determined by test.

Figure 9 shows the actual log E vs D curves for the left-hand path of the printer for the mask of Fig. 8, and with the correct filter pack in the undercorrection path.

Discrimination

The exposure control system of the printer is adjusted so that a normal daylight negative with good density and color distribution (no subject failure) produces a normal print, with the modulator shutters at the approximate midposition of the log E range. A clear-flash or tungsten-light-exposed negative has, on the average, about 0.30 less blue-light density relative to the green and red densities, than does a daylight-exposed negative.

Without undercorrection, the exposure control system of the printer would automatically correct for this difference to produce a normal print. With undercorrection set at a slope of -0.10, however, the log E at the paper plane of the blue component would be approximately 0.030 too high for a flash or tungsten-exposed negative. This would be equivalent to a print blue-density overcorrection of about 0.06. There would be, in other words, a little bit too much yellow on the print. To compensate for this effect, an electronic device called a "discriminator" has been installed on the encoding machine. It compares photoelectrically the integrated blue energy with the integrated red energy transmitted by the negative over the viewing aperture while the negative is being encoded for position or other reasons, and if the ratio of the two energies exceeds a certain value (as it would for flash), a punch is automatically set up to be released when the positioning punch is released. This puts another $\frac{1}{32}$-in. hole in the negative edge in line with the density correction and color correction holes.

This hole serves on the printer during the decoding operation to swing a 0.30 density filter 43 (Fig. 1) into the blue path of the illumination optics. This is equivalent to adding 0.30 density of blue component to the negative so that the blue modulator shutter would be forced to open wider as if it were seeing a daylight-exposed negative. Undercorrection, therefore, occurs as it would for a daylight picture of the same subject.

Negative Transport

As stated previously, the negative is positioned by means of a $\frac{1}{16}$-in. diameter hole punched in the opposite edge of each printable frame to the one containing the $\frac{1}{32}$-in. diameter holes for density and color-subject-failure correction.

Fast transport and reliable positioning accuracy are accomplished by means of a two-speed system. The negative is transported by means of a rubber-covered roller (Fig. 4) adjacent to the negative aperture. This pulls the film through. The roller is driven by a continuously operated electric motor against a constantly applied brake. Just behind the brake is a clutch which can be released magnetically to disengage the drive on the roller, allowing the brake to stop the film transport almost instantaneously. Just behind this clutch is another like the first which is bracketed by back gears containing also an overdrive clutch. During transport, both clutches are engaged, causing the negative to advance at the rate of 9 in./sec.

Light from the frame-positioning hole is picked up by a first photocell, Fig. 2, which causes the negative speed to be reduced from 9 in./sec to 1 in./sec by disengagement of the second of the two clutches referred to above. An instant later, the second photocell picks up light from the same hole, and the negative is stopped by disengagement of the first of the two clutches referred to above.

Continuous tests extending over periods of several days have shown, after statistical analyses, that the 3σ value of the transport system is $+\frac{1}{64}$ in.

Paper Transport

The paper transport is of conventional design. Seven-inch wide paper is transported over the two apertures by means of a rubber-covered roller whose half perimeter is equivalent to the length of transport desired. This so-called measuring roller is driven by a conventional half-revolution clutch whose pawl is withdrawn momentarily from a detent by a solenoid which is pulsed by electrical power at the moment transport is called for by the programming switch. When the clutch has rotated one-half revolution, the pawl drops by spring tension into a second detent which stops the measuring roller.

The transport system contains a device for automatically passing by a splice section in the paper. All other printing cycle functions are stopped by suitable interlocks during this operation.

In addition, there are markers to place a small graphite mark on the back of the paper on each frame for automatic chopping later, and another similar mark on the first print of each customer order to halt the chopper between customers' orders.

The latter mark is initiated by a single $\frac{1}{32}$-in. diameter negative hole, in line with the density and color-subject-failure correction holes, which has been placed there by the encoding operator. This is designated as the end-of-order mark.

Programming System

Programming is accomplished by a stepping switch. All positions of the stepping switch are revealed on the front panel of the printer by small indicator lamps. In certain positions, open contacts in the stepping switch permit it to dwell until certain functions have been completed. The completion of these functions provides a signal which advances the stepping switch to the next position.

The programming is briefly as follows:

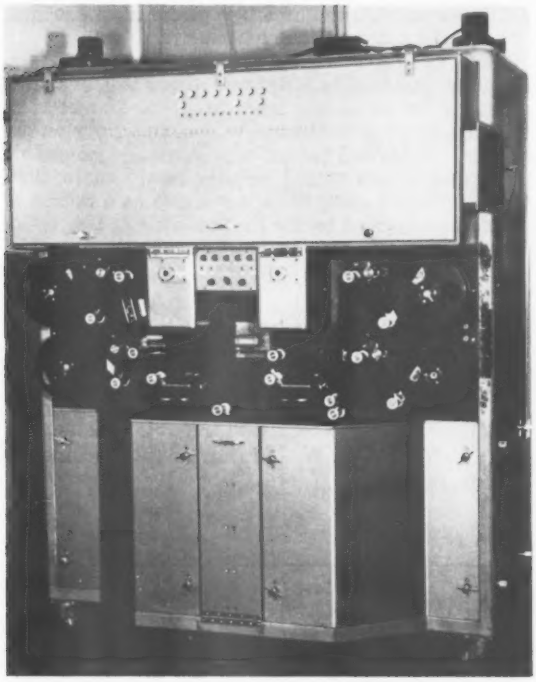

Fig. 10. Front view of printer. Paper compartment cover (top) contains lights showing stepping switch positions and decoding functions in operation, and switches for testing functions.

1. The negative gates are held open and all transports are started.
2. All transports are stopped and the negative gates are closed.
3. Paper markers are actuated, and density and color corrections are inserted into the exposure control system.
4. As soon as all six modulators are in printing position, the error signal detector permits the dowser shutters to open.
5. The dowser shutters are held open for 0.50 sec by means of an electronic timer.
6. The dowser shutters close, permitting the next printing cycle to begin.

Should a single function in either path fail, all operations are halted by suitable interlocks. Should either negative or paper run out or break, other interlocks bring the operations to a standstill.

If desired, printing on one path only can be accomplished by means of a selector switch.

On the front cover of the paper compartment (Fig. 10) there are illuminated numbered switches which can be used to intentionally stop the stepping switch in certain positions. When the stepping switch has been stopped in these various positions, there are additional illuminated switches which can be depressed to test each printer function controlled by the position.

Fig. 11. Close-up view of encoding machine.

Encoding

Figure 11 shows the encoding machine.

The prespliced negative roll is fed from left to right over an illuminated aperture where the operator can judge each picture for framing position and for subject-failure correction.

The negative is advanced by a motor-driven shaft containing a drive clutch which remains engaged until an electronic timer releases it. The operator can, at will, control the time interval of the timer so that the negative advance is approximately equivalent to one frame.

By means of the hand wheel shown at left, the final fractional movement for best framing can be accomplished manually by the operator. A button on the right-hand panel permits the operator to advance the negative continuously and rapidly to pass up splices or unprintable frames. On the panel to the right are rows of buttons which set up pneumatically operated punches. The bottom row is for density corrections. The three upper rows are for color corrections, each row for a color component. Color corrections, if any, are always set up first. When the operator depresses one of the density correction buttons which he must, even if it is the normal button, all punches are operated and the negative is transported. While the negative is being framed and judged, the light transmitted by the negative is being read by the discriminator above, which instantly sets up a punch if the negative has been clear-flash or tungsten exposed.

Any depressed button may be released by de-

pressing another in the same row. All buttons are released at start of transport. There is also a button for end-of-order.

Summary

The complete printing cycle time of the printer is 1.20 sec for every two prints. With an average number of unprintable frames, paper splices, and negative splices, all of which are passed up by the printer and, therefore, cause momentary interruptions in the printing cycle, the printer produces 5000 prints/hour.

To do this on a continuous basis, four encoding machines are required, because experience indicates that an operator can encode between 1200 and 1500 frames/hour.

The 115-v printing lamps are operated at 95 v, which should insure long life; and the reference lamp is operated at one-third the rated voltage, with a voltage regulator.

Should any function in either path fail, the printer operation is automatically halted.

Each printable negative picture has one $\frac{1}{16}$-in. diameter positioning hole, and there are available positions for 15 coding holes of $\frac{1}{32}$-in. diameter on the opposite edge to control various functions on the printer. A normal picture would require no coding holes and others would require rarely more than three. These coding holes serve also as a record of corrections applied to the first printing. The $\frac{1}{16}$-in. diameter positioning hole is utilized later to control an automatic negative chopper.

Acknowledgments

The authors wish to acknowledge, gratefully, the encouragement and freedom given by the Technicolor management, and the able assistance of Donn Kefes and G. W. Mergens of the Technicolor organization.

1960 Rapid Processing Symposium 14–15 October

Shoreham Hotel, Washington, D.C.

The Society will hold a Rapid Processing Symposium at the Shoreham Hotel, Washington, D.C., on October 14 and 15 of this year, in cooperation with the Fifth International High-Speed Congress, which will be held in Washington October 16–22. A major goal of the Symposium is the exchange of information relative to: compact, simplified photoprocessing equipment with short access time; special techniques associated with the development and design, the photographic chemistry involved, and the manner of utilization; and, possibly, new features in the design and construction of larger processing machines, and advances in processing methods and control techniques. Exhibit space will be available at a nominal fee for the display and operation of related equipment.

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A Novel Method for Characterizing Photographic Gelatin

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Recent studies in these laboratories have shown that the polymerization of vinyl monomers upon illumination is promoted by silver salts. When such photopolymerizations are carried out in aqueous gelatin solutions, the type and nature of the gelatin profoundly affects the initiation period of the reaction. This initiation period is evaluated from a plot of the temperature of the reaction mixture against total exposure. At a given illumination intensity, the time measured before a sharp temperature increase occurs is shortened in the presence of photographically "active" gelatins. Conversely, photographically "restrained" gelatins lengthen the initiation period. Photographic emulsion additives such as sensitizers and antifoggants can be studied and evaluated in model systems containing monomers, catalyst, and "inert" gelatin. It is felt that this reaction may be developed into an interesting and novel method of characterizing photographic gelatins.

The need for a simple and rapid characterization of the photographic properties of gelatin without the preparation of a trial emulsion has been documented in the photographic literature. Earlier attempts to determine the active impurity of photographic gelatins such as sensitizing sulfur compounds have been made by Vogel, Luther, Sheppard, Steigmann, Abribat, and others. It is well known that the sensitizing effects of gelatin impurities are counteracted by other impurities occurring in commercial gelatins which are generally referred to as restrainers. In most cases it is impossible to evaluate readily the interplay of these substances in photographic emulsions except for making a trial emulsion or resorting to an evaluation of activators and restrainers separately. More recently, H. Ammann-Brass[1] published a method for characterizing gelatins by measuring turbidity due to grain growth of silver/cadmium chloride, a technique which allows certain conclusions to be drawn concerning the photographic properties of gelatin.

We were looking for a method which would permit study of the change of the light sensitivity of silver halide rather than its grain growth as a direct result of the interactions of gelatin impurities with the silver halide, preferably without cumbersome evaluation by sensitometry and chemical processing. This paper describes a model system which we believe shows promise for such evaluation.

It was observed recently in the Ansco Laboratories that silver halide gelatin emulsions can cause polymerization of acrylamide upon exposure to light. This polymerization process was followed by plotting the temperature of the exothermic reaction mixture against the time at constant light intensity from a projection lamp. As in many polymerization systems, particularly if a crosslinking agent is added to the monomer solution, the temperature initially rises slowly until the gelation point is reached. Since the system is not adiabatic, the temperature rise is indicative of — but not proportional to — the extent of the polymerization. At this point, the temperature rises rapidly, and polymerization is usually complete within a short time. We first prepared precipitates of the various types and concentrations of silver halide in inertized gelatin to which was added a solution containing as a monomer 59% acrylamide and 2% of a crosslinking agent (N,N'-methylene-bis-acrylamide).

Figure 1 shows the experimental exposure arrangement. The time lapse from the start of the exposure up to the gelation point is called the initiation period. At a given irradiation intensity, the time interval between the start and the sharp increase in temperature is affected by the type of silver halide and its concentration and by the nature of the gelatin in which the silver halide is dispersed. As will be shown later, the initiation period is shortened when photographically active gelatins are used and,

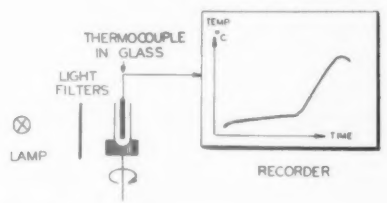

Fig. 1. Experimental setup.

Presented at the Colloque International de Photographie Scientifique, Liège, Belgium, 14–19 September 1959. Received 1 February 1960.

1. H. Ammann-Brass, *Kolloid. Z.*, **110**: 1 (1948).

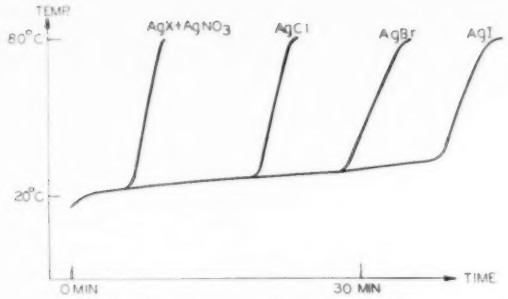

Fig. 2. Comparison of silver halides.

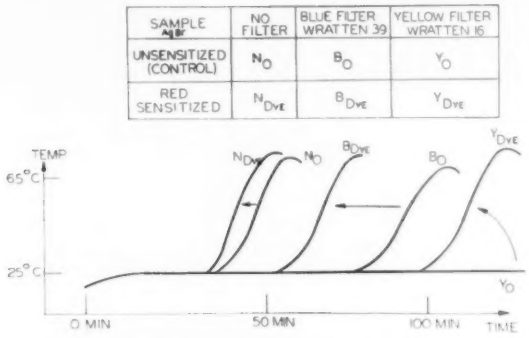

Fig. 3. Effect of sensitizing dye.

conversely, it is lengthened when photographically restrained gelatins are used. A carefully inertized and deionized gelatin was therefore selected as a standard.

Table I shows a typical mixture of the aqueous gel/monomer composition with the silver halide catalyst (see p. 154).

Figure 2 compares the results with various silver halide emulsions. It was noted that silver chloride at any given concentration yields a shorter initiation period than emulsions of silver bromide or silver iodide. Furthermore, emulsions of silver chloride precipitated in the presence of an excess of silver nitrate showed an even shorter initiation period. In the latter case, however, the photolytic reduction of silver occurs too rapidly, particularly at higher concentration, so that we elected to work with halide ion excess because this system shows a better spread of our temperature curves, as indicated in the figures. Furthermore, when working with a halide ion excess (e.g., $AgBr/Br^-$), the influence of halide ions which may be present in commercial gelatins is eliminated or minimized.

It is known, from making emulsions, that the chemical interaction of gelatin impurities with silver halide controls sensitivity by either enhancing or suppressing the formation of sensitivity or fog specks. The literature indicates that the spectral absorption of the silver halide is simultaneously extended towards the longer wavelengths.[2] The silver halides were either precipitated in test tubes under conditions closely resembling those of actual emulsion making or added in the form of a washed fine-grain silver halide emulsion. In addition, conventionally prepared photographic emulsions, washed, not-ripened or ripened, served well simply by adding the standard acrylamide solution to them. It seems, therefore, justified to ascribe the observed acceleration or retardation of the photopolymerization reaction to the same interactions of gelatin with silver halide which play an important role in conventional emulsion making. In other words, any alteration in the light sensitivity of the silver halide gelatin emulsion produced by gelatin impurities, or by other emulsion additives, will also influence its efficiency in photopolymerization. Analogously, the photolysis of silver halide was expected to be enhanced by a bromine-acceptor-effect of the impurities or by extension of the spectral absorption by dye or other additives.[3]

To support this statement further, we have studied the effect of an optical sensitizer of the cyanine class (3,3′-diethyl-9-methylthiacarbocyanine) and exposed the model solution through selected filters (Fig. 3). The results conform with the well-known optical sensitizing effect of this dye on silver halide. If the natural blue sensitivity of the silver halide is screened off by a yellow filter (Wratten 16), no photopolymerization occurs in the absence of a red sensitizer; conversely, if the dye is present, polymerization takes place. Experimental controls indicated that the same quantity of dye without silver halide does not induce photopolymerization.

Figure 4 shows the sensitizing effect of a typical sulfur sensitizer such as thiourea on silver halide. If the reaction vessel is charged with an unripened washed pure silver bromide emulsion, and a small

2. a. C. E. K. Mees, *The Theory of the Photographic Process*, rev. ed., New York, Macmillan, 1954, p. 352.
b. K. V. Chibissov, *Z. wiss. Phot.*, **51**: 89 (1956); ——, *J. Phot. Soc.*, **7**: 41 (1959).

3. Mees, *op. cit.*, p. 481.

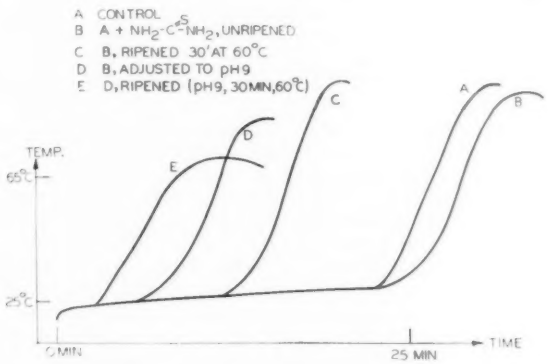

Fig. 4. Effect of thiourea. Curve A—control; Curve B—A + thiourea, unripened; Curve C—B ripened 30 min at 60°C; Curve D—B adjusted to pH 9; Curve E—D ripened at pH 9 for 30 min at 60°C.

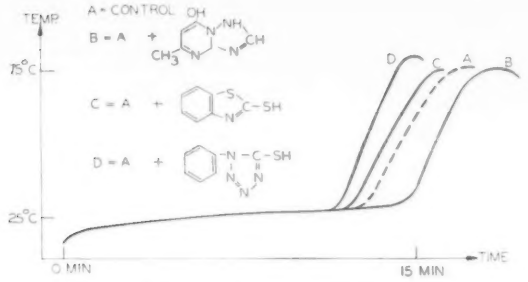

Fig. 5. Effects of conventional restrainers.

quantity of thiourea or thiourea derivatives is added (25 ppm of gelatin), the sensitizing effect of thiourea is again indicated by a shortened initiation period. It is of special interest to note that when thiourea is added to a silver bromide emulsion at an acid pH and at room temperature, the initiation period first increases (Curve B), presumably due to the formation of an addition compound of silver halide with thiourea.[4] If this complex on the silver halide surface is subsequently broken down to silver sulfide, either by changing the pH to the alkaline side, or by a digestion at elevated temperature at an acid pH or by the combination of both measures, the initiation period is substantially shortened (Curves C, D, and E).

The influence of certain restraining or stabilizing compounds on the photocatalytic activity of the silver halide is shown in Fig. 5. A typical stabilizing or ripening restraining agent such as 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (triazaindolizine)[5] always increases the initiation period, i.e., restrains the photopolymerization. When heterocyclic mercapto compounds such as the 2-mercaptobenzothiazole or 5-mercapto-1-phenyltetrazole are added, we observe that these mercapto compounds accelerate photopolymerization when present in low concentrations and retard it only when large doses are added. G. Kraft in 1933[6] first described a mild sensitizing effect of mercapto compounds on the photolysis of silver halides, and interpreted this as being due to their action as bromine acceptors. In order to examine the influence of bromine acceptors in our system, we added a small quantity of sodium nitrite.

From Fig. 6, it is evident that the known effect of nitrites on photolysis by increasing the quantum yield[7] is clearly paralleled here by a distinct shortening of the initiation time of photopolymerization, at the same time slowing the propagation of the polymerization as evidenced by the change of the slope of the curve.

4. Mees, *op. cit.*, p. 90.
5. C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. Van Allan, *J. Org. Chem.*, **24:** 782 (1959), Formula XVIII.
6. G. Kraft, *Z. wiss. Phot.*, **31:** 329 (1933).
7. Mees, *op. cit.*, pp. 124–125.

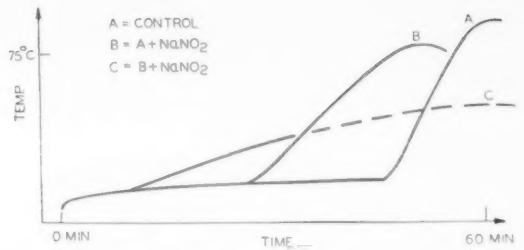

Fig. 6. Effects of sodium nitrite. Curve A—control (2.0 ml 4% gelatin solution, 0.15 ml 0.1N $AgNO_3$, 0.12 ml 0.1N NaBr, and 5.0 ml monomer solution); Curve B—A + 0.476 mg $NaNO_2$; Curve C—A + 0.952 mg $NaNO_2$.

Finally, we selected several gelatins which had been classified on the basis of emulsion trials and by means of the Ammann turbidity curves as "highly active," "restrained," and "inert." Figure 7 shows the effect of these gelatins (5% solution) on unripened silver bromide. We were able with our method to confirm the gelatin classification obtained by the other methods mentioned above.

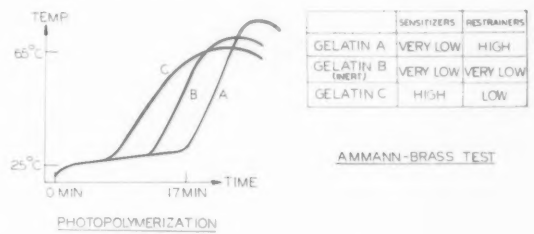

Fig. 7. Comparison of gelatins.

We realize it may be premature to claim that our system will lend itself to routine gelatin classification, but preliminary results look promising.

We believe that the new method described above will permit the study of the mechanism of photolysis and the intrinsic photographic sensitivity of silver halides. The chief advantage of our method rests on its relative simplicity and the independence of effects normally introduced by processing solutions.

Acknowledgment

The authors wish to acknowledge the stimulating discussions in the furtherance of this program with Dr. F. J. Kaszuba, Steven Levinos, and Dr. A. K. Schwerin, all of the Ansco Research Laboratories.

Experimental Procedures

1. Silver halide precipitated in the reactor

2.5% gelatin solution	4.00 ml
0.1 normal NaCl	0.25 ml

are mixed in light into a test tube.

0.1 normal $AgNO_3$	0.20 ml

was added at 25° in a darkened room (red light, a 15-w lamp in a "Kodak Adjustable Safelight" with a 1A Wratten Filter).

After the addition, the mixture was stirred by hand with a glass rod for 60 sec at room temperature. Then

"Monomer solution" . . . . . 4.00 ml

was added, and the mixture was stirred again at room temperature for 120 sec. The mixture was then, for the duration of the experiment, continually exposed to a 100-w tungsten lamp (a GE-100T-8½-8 microscope lamp, 120-v, with a CC 13 filament, base down, from General Electric Photo Lamp Department, Nela Park, Cleveland 12, Ohio). The distance from the glass surface of the lamp to the center of the test tube was 10 cm.

The "Monomer solution" had the composition given in Table I.

TABLE I

Composition of Polymerizable Mixture

Gelatin (about 1–5%)	4.00 ml
0.1 *N* sodium chloride	0.25 ml
0.1 *N* silver nitrate	0.25 ml
Monomer solution	4.00 ml

Composition of Monomer Solution

Acrylamide (CH_2:$CHCONH_2$) .	180.00 grams =	59%
N,N′-Methylene-bis-acrylamide (CH_2:$CHCONHCH_2NHCO$-CH:CH_2)	7.00 grams =	2%
Water	120.00 ml =	39%
Total		100%

2. Silver halide added in the form of a washed photographic emulsion

A slow, fine-grain, unripened emulsion was prepared by using an inertized and deionized gelatin.

Solution A	H_2O	100.0 ml
	NaCl	18.87 grams
	or KBr	38.50 grams
Solution B	H_2O	100.0 ml
	$AgNO_3$	50.0 grams
Solution C	H_2O	800.0 ml
	Gelatin	100.0 grams
	HNO_3 conc. . . .	1.00 ml

Solutions A and B were run simultaneously into Solution C over a period of 60 sec at 34°C. The addition was made in such a manner that NaCl was present in excess at all times. After the addition was complete, the emulsion was immediately chilled, noodled, and washed for 3 hours with 12°C water. An analysis showed 21.65 grams of metallic silver per kilogram of emulsion.

At the time of the submission of this manuscript, our method consists of utilizing the following experimental mixture:

4% gelatin (to be tested)	2.00 ml
Washed AgBr emulsion	0.20 ml
"Monomer solution"	5.00 ml

Photographic additives are added after the gelatin and silver halide emulsion have been mixed. Any ripening is carried out at this point. The temperature is adjusted to 30°C, the monomer solution added at 30°C, and the suspension immediately exposed to the projection lamp as described above.

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A Demonstration of Color Perception with Abridged Color-Projection Systems

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The way primary colors combine to produce colored pictures was demonstrated. The range of colors perceived when less than three primaries were used was attributed to the known psychological effects of induction by contrast, color constancy by discounting of the illuminant, and memory color, all of which were demonstrated. The reproduction characteristics of two-color systems were demonstrated, and a direct comparison was made between a two-color and a three-color reproduction of the same scene.

Classical Color Theory

The ancient Greeks knew that all the hues of nature could be obtained by mixing red, yellow, and blue paint. In 1666, Isaac Newton did his famous experiments with a prism. He found that sunlight could be dispersed into a spectrum of violet, indigo, blue, green, yellow, orange, and red. By means of a second prism, he was able to recombine these colors to make sunlight. A few other experiments convinced him that the colors of things were caused by selective absorption of various parts of the spectrum and that the colors of lights depended upon their spectral content. He did not speak in terms of wavelengths because he did not believe in the wave theory of light.

In 1802, Thomas Young, who did believe in the wave theory of light and did much to advance it, presented his theory of color vision. He reasoned this way: if all hues can be obtained by mixing red, green, and blue lights, and if the eye cannot see the components after they are mixed, then the eye needs only three kinds of receptors—some tuned to red, some tuned to green, and some tuned to blue. Just as primary lights could be mixed to produce various other lights, so the perceptions of the primary lights would be blended to produce various other color perceptions.

If we were to use the term "classical color theory," this is where we would draw the line. But, of course, this is only the beginning. It gives a first approximation upon which we make refinements.

Photography became generally known in 1839. At first, of course, it was just black-and-white photography. Just sixteen years later, in a paper on color vision, Maxwell drew a purely hypothetical example from the art of photography to illustrate Young's theory.[29*] Though this was primarily an example to clarify a discussion of the theory of vision, it was, in fact, the invention of color photography. Speaking of Young's theory, he said, "This theory of colour may be illustrated by a supposed case taken from the art of photography. Let it be required to ascertain the colours of a landscape, by means of impressions taken on a preparation equally sensitive to rays of every colour.

"Let a plate of red glass be placed before the camera, and an impression taken. The positive of this will be transparent wherever the red light has been abundant in the landscape, and opaque where it has been wanting. Let it now be put in a magic lantern, along with the red glass, and a red picture will be thrown on the screen.

"Let this operation be repeated with a green and a violet glass, and by means of three magic lanterns, let the three images be superimposed on the screen. The colour of any point on the screen will then depend on that of the corresponding point of the landscape; and, by properly adjusting the intensities of the light, etc., a complete copy of the landscape, as far as visible colour is concerned, will be thrown on the screen."

Later, he obtained the services of Thomas Sutton, the photographer, to carry out this suggestion and on May 17, 1861, he successfully demonstrated such a system.[30]

The Two-Color Phenomenon

Toward the end of the nineteenth century, Louis Ducos du Hauron developed three-color separation to a fine art and made beautiful color prints, using red, yellow, and blue pigments. In 1895, he made a most interesting observation.[9] The following is translated from his article in the December 10, 1895, issue of *Photo-Revue Africaine:*

"During my last researches I have discovered a marvelous law by virtue of which an image, composed of only two monochromes, is capable of pro-

Presented at the National Conference, Chicago, 27 October 1959. Received 22 December 1959.

* Specific literature references are included in the bibliography at the end of this paper.

ducing on the visual organs, under certain conditions, a colored sensation as complete as the trichromatic images, which I have already obtained. The novelty consists in eliminating the yellow monochrome, but taking and superimposing the red and blue monochromes as usual. . . . The phenomenon, that I have suggested, requires one condition and that is that the double image should be examined, not by white light and plenty of it like bright daylight, but rather by weak daylight and just enough to see the subject, or better still by the yellow light of candles or lamps. Viewing the result by daylight is possible, with very great reduction of the light, if the image is produced on a yellow or gray support. It should be noted that, under these conditions, the yellow sensation cannot be attributed to the yellow illumination nor the yellowish surface on which the print is made, in fact the white parts of the scene are rendered as white while the yellows are rendered as yellow. Observers actually believe that they see the three colors where they ought to be, although they know that they are actually absent."

He reprinted this article in its entirety in his famous book on color photography written in collaboration with his brother in 1897, and this passage is quoted by Wall in his well-known *History of Three-Color Photography*, so it is not quite as obscure as might be supposed from the original reference.[9,36]

That was the beginning of two-color photography. During the first third of this century, a variety of two-color systems were patented and a number were used in the motion picture industry. Generally, separate pictures were taken through red and greenish-blue filters and projected through similar filters, but in some cases, as in the Fox, Hickey, and Kinemacolor patent, the picture taken through the green filter was projected with no filter, just incandescent lamp light.[15] Wall describes many two-primary systems in his history of color photography.[36] In 1924, Mannes and Godowsky patented their first work on a multiple-layer film which eventually led to the development of Kodachrome.[28] When this three-layer film came on the market in 1935, it was so much superior to the two-color systems that the latter fell pretty much into disuse and the emphasis has been on three-color systems ever since.

Perhaps we have not seen the last vestiges of two-color systems yet. Recently, Land published the most extensive description of two-color experiments in the literature.[25,26,27] This has generated a resurgence of popular interest in the field. My interest in this subject is not in applications but in explanations. Many phenomena which are vividly apparent in two-color displays of pictures are simply inconsistent with the classical theory of Newton and Young, which applies to the color of a spot of light with a dark surround.

Psychological Factors

Fortunately, a great deal has been learned since 1802. We have known for years that the color that we perceive depends upon many factors—not just the spectral quality of the light coming from a given area. In fact, Helmholtz cites 178 references to works bearing on the subject of contrast between the years 1651 and 1894.[16]

You have probably had the experience of staring at a red spot on white paper and then shifting your gaze to a white surface. You then see a blue-green spot. This is called an after-image and this color is called the after-image complementary of red. Every hue has an after-image complementary.

When red and green are placed side by side the red looks redder and the green looks greener. This effect is known as simultaneous contrast.

If we look first at red, then at green, the same sort of thing happens. We refer to this effect as successive contrast. Actually, these two effects are not easy to separate because, when two colors are in the field of view, the eye scans back and forth so that successive contrast effects are operating.

The level of illumination is also involved. To demonstrate this, try arranging 64 or so different colored crayons in a systemmatic way by the light of the moon.

The state of adaptation of your eyes plays an important role, as can easily be demonstrated.

All of these effects apply as well to spots of light as to colored objects but when we view objects or images of objects, the astonishing influence of the interpretive portion of the visual system makes itself fully apparent.

Have you ever driven down an asphalt road into the setting sun? "Classical theory" would tell you that a road of gold lay before you. But that is not what you perceived. In spite of the blinding glare of yellow and red light, what you perceived was a shiny black surface. This is not a matter of reasoning—it happens automatically and is known as "discounting the illuminant." Every time you look at a group of objects, your visual system instantly appraises the illuminant and, as we say, "you see it in that light." Your visual system acts something like a spectrophotometer which "looks at" the source and then at the object, and takes the ratio of the amounts of light to find the reflectance of the object.

We discount reflections. For example, when you are looking into a shop window, you don't notice the reflection of the blue sky in the window; you discount that and perceive the colors of the merchandise inside.

When the amount of color information is scant, we may perceive the colors of objects as we remember them.

Some of these effects were known to Leonardo da Vinci in the 15th century.[5] Helmholtz described many of them in his celebrated treatise on physiological optics, but mostly only qualitatively.[17] In the years between the two great wars in the first half of this century a number of psycho-physicists, notably Helson and Judd, armed with new quantitative methods, attacked the problem of object color perception with considerable success.[18,19,20,22] Still there is no unified theory of all these effects. How are you going to take into account what a person re-

members or whether he is interested in the reflection in the window or the merchandise inside? There is no simple accounting for these things, but in a paper written in 1939, Judd did unify some of these factors in a set of equations for computing perceived object color under a wide variety of conditions.[22]

Let me describe this formulation by a geographical analogy. In the United States we have eastern states and western states, "the East" and "the West." But to the New Yorker, Cincinnati is out west; in Cincinnati, Chicago is out west; and in Chicago, Denver is out west. Now in Judd's mathematical map of colors, there are states—states of adaptation. Just as the directions to places depend upon your location, so the colors perceived depend upon your state of adaptation. If your eyes are adapted to red light, a light which is a little less red may look green. This sounds unbelievable but it is easily demonstrated. Judd's formulas permit the computation of the perceived colors of objects in colored illumination or in two-color projection systems.[23]

Demonstrations*

(1) A three-color separation picture of familiar grocery items was shown, using the method described by Maxwell a hundred years ago. The photographs were taken on Kodak Plus-X film and were printed on Cramer Class II Contrast Lantern Slide Plates. The camera filters were the customary color separation set: Wratten 25 red, Wratten 58 green, and Wratten 47 blue. The projection filters were the customary tungsten color-projection set: Wratten 29 red, Wratten 61 green, and Wratten 47 blue. Colors seen were red, yellow, pale green, brown, reddish purple, yellowish orange, blue, black, and white. Images were shown separately and in combination.

(2) The intensities of the red and blue projector lamps were varied to show the appearance of such a scene by the light of the setting sun and by light from an overcast sky. The colors of objects appeared to remain constant while the illumination seemed to change. It was pointed out that color constancy is only one of many known psychological constancy effects. For example, the screen was perceived to remain constant in location even though the observers looked about or shook their heads.

(3) The green filter was removed and the lamp in the projector with the green separation positive was reduced in intensity to restore the original screen luminance. The green objects again looked green, but less saturated, even though there was no green filter in use. The other colors remained more or less constant. The red and blue filters made the average color of the screen magenta so the incandescent-lamp light appeared green by contrast.

(4) In making prints, Hauron found that he could get some semblance of full color when the yellow image was deleted. His was a subtractive system—that is, his pigments were colored because they selectively absorbed or subtracted light. Here we have an additive system because each projector adds light of a different color. Since yellow pigments subtract blue light, they control the blue component of the picture; in the present case the blue component is controlled by the blue projector. If we reduce the intensity of the blue projector to zero, we are left with red and "white." Members of the audience reported seeing red, green, yellow, white, black, purplish red, and in a few cases brown and blue. Here the visual system is adapted to reddish light and the parts which are lighted by incandescent-lamp light appear green or bluish-green.

The audience was asked to cover one eye and continue to view the scene with the other. It was explained that the visual system undergoes some extremely rapid adaptation and that this is followed by a more gradual process.[31,32] After about a minute, the audience was asked to shift quickly from one eye to the other and compare the two views. It was readily apparent that the view "at first glance" was far less colorful than it was to the eye which had undergone adaptation for some time.

As the screen luminance was gradually decreased there was, at first, an increase in the apparent saturations of the colors. The saturation became a maximum and then began to decrease as the screen luminance decreased. As the screen luminance was reduced, the audience was asked if particular colors were seen. At a very low luminance, the red projector was turned off. Positive responses continued to come from the audience. It appeared that a majority of the audience saw some chromatic color, the yellow color of mustard being most persistent. Some saw red, green, blue, and purplish red. It was then revealed that the image was black-and-white with no filters. The image was made considerably brighter and many people still saw various hues. This is an example of memory color. Most of the chromatic color seen in the black-and-white slide is attributable to memory color, but not all of it. Judd's formulas predict that when a black-and-white image is projected with yellowish incandescent lamp light, some yellow should be seen in the lighter areas. A description was given of laboratory experience with American and Dutch observers who were shown this black-and-white picture at low screen luminance. Some Americans, having thorough familiarity with the objects pictured, described the scene in full color. The foreign observer saw more colors after experience with the real colors than at first, when his observations corresponded to the predictions of Judd's formulas. Thus the importance of memory color was shown.

(5) To eliminate some of the complicating factors involved in object color perception, we turned next to a three-color separation of a color chart. The chart was a circle of 20 chips of uniform saturation in

* The demonstrations described in this section were carried out by the author as part of his presentation of the paper at the 1959 National Conference.

the usual order of hue and a disordered array of the same kind of chips within the circle, all on a medium grey background. The same progression of abridgement was employed as before—first red, green, and blue, then red, "white," and blue, and finally, red and "white." The decrease in saturation and the lack of distinction between colors progressed with abridgement. The gray regions in the circle, inevitably associated with two-primary systems, were pointed out to the observers.

(6) To obtain even more abstract viewing conditions, we next considered spots of light with no images at all. We saw that red and green light can be combined in all proportions to obtain the series of hues running through red, orange, yellow, yellowish green, and green. Bear in mind that we were mixing light, not pigments. This is an additive system, not a subtractive system. Red and blue can be combined to obtain the series running through magenta. Blue and green can be combined to give the series running through cyan.

(7) The three beams were balanced to provide a spot of light that looked like daylight. The lens of the green projector was covered and the audience was asked to concentrate on the resulting magenta spot and to observe the rapid changes when the green light was suddenly returned. A very rapid adaptation process was observed in which the spot suddenly appeared green due to successive contrast and then returned to daylight color within a half second or so.

(8) The beams were adjusted so that the red, green, and blue spots were partially separate and partially overlapping. The red, green, and blue primaries and the results of mixture were seen simultaneously, the red and green producing yellow, the green and blue producing cyan, the blue and red producing magenta, and all three together producing light similar in quality to daylight.

(9) We removed the green filter, as we did in the case of the picture, and saw that the visual system readily adapts to this situation and we could again see the green color. Colors such as this which we would not have seen except for the influence of adjacent colored areas are called "induced colors." We saw not only the induced green color, but we saw that the apparent mixture of the induced color with "real colors" produced yellow and cyan; that is, in mixture, the induced green produced the same apparent hues as the real green.

(10) The blue projector was turned off and the remaining red and "white" circles were turned to the left of the screen. The circles were made nearly coincident, a red crescent remaining at the left and a crescent of incandescent-lamp light remaining at the right. Under these conditions, the crescent of incandescent-lamp light appeared green and the intersection appeared pinkish-yellow or yellow. With the remaining projector, a circular spot of green light was placed on the right side of the screen and the audience was invited to compare the "green crescent" with the green circle. The two were seen to be very similar in color though not identical in hue. Thus it was shown that an induced color and a real color of the same kind can be compared in the same field of view. The spot of incandescent-lamp light was moved away from the red spot and placed beside the green spot. It was then seen that the incandescent-lamp light and the real green light were very different in color. When the spot of incandescent-lamp light was placed in partial coincidence with the green spot and the green spot was made sufficiently bright, the remaining crescent of incandescent-lamp light appeared rosy pink. Thus the incandescent-lamp light could appear green or pink, depending upon the color of the adjacent area.

(11) The entire screen was illuminated uniformly by a mixture of red light from one projector and incandescent-lamp light from another. A man was asked to stand in front of the projectors and cast shadows on the screen. The shadow cast by the red-light projector was illuminated by the incandescent-lamp light and appeared quite green. The other shadow appeared very red. These are known as "colored shadows" and have been known for over a century. Again it is seen that when the visual system is adapted to reddish light, the incandescent-lamp light looks green.

(12) I have often heard it said or implied recently that you can't tell a projected two-color picture from a projected Kodachrome or Ektachrome transparency. One way to find out is to place them side by side and see for yourself. A red-and-white two-color picture of a vase of flowers was shown on one half of the screen. Since flowers can be almost any color, the observers had no way of knowing what the colors were in the original. The audience was asked to look at the various flowers and bear in mind the colors perceived. A Kodachrome picture of the same flowers was shown on the other half of the screen. The average screen brightness was adjusted to match that of the two-color display. There were pale blue flowers which looked yellow in the two-color display and there were pale cream tints in some of the flowers which were lost in the abridged system. Rich purple flowers looked purplish brown and, in general, the saturation was very low in the abridged system. This is a poor example of what this two-color system can do at best, but it is a good example of what it will do with pale yellows, blues, and purples, which are frequently encountered in practical photography, where we often cannot choose the colors of our subject.

Conclusions

Two-color systems have a long history. The known psychological effects of induction by contrast, color constancy by discounting of the illuminant, and memory color adequately account for the colors perceived. The first order effects can be observed with spots of light as well as with images or objects and were quantitatively formulated twenty years ago.

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The Bromination of Gelatin

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A fine-ground gelatin has been observed to undergo a substitution reaction with molecular bromine at room temperature. In the pressure range of 7–9 microns of halogen and in the presence of excess gelatin, the reaction is characterized by the slow evolution of hydrogen bromide. Analytical results indicate the formation of one mole of hydrogen bromide for each mole of bromine reacted. Bromine atoms appear to have a negligible effect upon the rate. Addition of known quantities of moisture to the gelatin greatly accelerates the reaction. On the basis of experiments performed at temperatures from 1.5 to 66.2°C, an activation energy of approximately 3.1 ± 0.6 kcal/mole was obtained.

Although contradictory statements have been made concerning the effect of the water content of gelatin upon photographic sensitivity, there is evidence that halogen acceptance is dependent upon the moisture content of the vehicle.[1] Experiments by Berg[2] showed that relatively dry gelatin surrounding photographic emulsion grains is unable to cope with the bromine released, and only in these cases is photographic sensitivity improved by bromine acceptance, such as by mere moistening of the layer or addition of a halogen acceptor.

For print-out silver formation in a photographic layer, it has been shown[3] that desensitization occurs by heating at 80°C for 90–120 min. This desensitization is attributed to loss of water during heating and consequent loss of halogen-acceptor action by gelatin. Sensitivity was restored by storage of the photographic plate in a desiccator over water for a period of one hour. Prolonged storage over water caused loss of sensitivity in both the heated and the unheated material.

Hamilton, Hamm, and Brady,[4] by the use of simultaneous pulses of light and voltage, studied the motion of electrons and holes in photographic silver halide crystals and showed that positive holes at the print-out level are mobile and possibly react readily with gelatin. Electron micrographs revealed a diffuse cloud of matter of higher electron-scattering power outside the periphery of the grain, on the side opposite the silver deposit. This cloud is absent in unexposed grains or those exposed only to latent-image level and is symmetrically located around the entire grain if the print-out exposure is made without an electrical field. The authors reported that this diffuse cloud consisted of bromogelatin, resulting when positive holes, displaced during the pulsed exposure to the edge of the grain, lead to the escape of bromine atoms, at least some of which combined with gelatin to form the complex. Unpublished results by the investigators indicate that the bromine is irreversibly held by the gelatin in this diffuse cloud.

In an earlier study, Slater-Price[5] suggested a mechanism for the reaction between gelatin and bromine. The mechanism was dependent upon the hydrolysis of molecular bromine to form bromide and hypobromite ions. It was suggested that hypobromite was the ion more probably reacting with gelatin. The mechanism also included a molecular bromine and gelatin reaction.

All previous measurements of the reaction between the protein and halogen were made with concentrations of bromine of the order of 10^{-4} mole or larger, a concentration far exceeding that estimated to be released under conditions of low-intensity exposures.

The purpose of the present investigation was to study the role of atomic and molecular bromine in halogen acceptance by gelatin in a system capable of detecting 1.24×10^{12} molecules per cubic centimeter. Also to be investigated was the effect of low concentrations of water in the gelatin upon the reaction.

Experimental Materials and Procedure

The gelatin used in this study was an Eastman Kodak Company low-activity, fine-ground bone gelatin of pH 5.6. Deamination of the material had been accomplished by treatment with acidified sodium nitrite solution. The particle size was 100-mesh or smaller. The bromine employed in the experiments was Baker and Adamson Reagent Grade

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1. S. E. Sheppard and C. L. Graham, *J. Franklin Inst.*, **230:** 619 (1940).
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5. T. Slater-Price, *Phot. J.*, **71:** 59 (1931).

TABLE I — Rate of Reaction of Vacuum-Dried Gelatin with Bromine at Room Temperature

Experiment No.	Weight of gelatin (mg)	*P_0 (Br_2) (microns)	Time (min)	μg Br/min/gram of gelatin	μg Br in volatile gas/min/gram of gelatin	Total μg Br reacted/min/gram of gelatin
16	21.5	9.50	40.0	2.4	2.7	5.1
17	18.4	9.05	50.0	1.1	3.4	4.5
18	27.6	3.92	20.0	2.4	3.6	6.0
19	36.8	7.58	25.0	2.2	—	—
21	31.5	8.70	30.0	2.2	2.8	5.0

* P_0 = initial pressure.

which had been purified over triply distilled sodium.[6] Prior to reaction, the material was degassed at −196° C and then trap-distilled from −80° to −196°.

An experiment was performed in the following manner: The gelatin, contained in a small-volume Pyrex-glass reaction tube, was vacuum-dried and then transferred to a known reaction volume, and the system evacuated to a pressure of 10^{-6} mm of mercury or less. A known reaction quantity of bromine, as measured by a calibrated Pirani gauge, was then introduced through a break seal exposing the gelatin to the halogen. The rate of the reaction was followed manometrically with the Pirani gauge. In some instances the effect of water vapor on the reaction between molecular bromine and gelatin was of interest, and two general methods were used to introduce moisture. First, water stored in a bulb attached to the vacuum system was deaerated at −112°C, and a given concentration, as measured by the Pirani gauge, was expanded into the reaction volume and permitted to equilibrate with the dried gelatin. The second method involved treating gelatin samples over saturated salt solutions and rapidly transferring them to the vacuum line. Degassing of samples was accomplished as previously mentioned, after which given concentrations of halogen were reacted with the moistened gelatin. A detailed account of the vacuum apparatus, calibrations, experimental errors, and methods is given in the Appendix.

Experimental Results

A. *Experiments in the Dry State*

Since the reaction was characterized by a slow increase in pressure, analytical techniques were sought to establish the product or products of the reaction. To determine whether noncondensables were present in the product, the reaction mixture, after a given time, was condensed into a finger, which was at −196°C. In two experiments, with 7–8 microns' initial pressures of halogen, carried to more than 20-min reaction time, it was possible to condense, on the average, more than 99% of the reaction mixture. The experiments showed that residual gases, CO, H_2, etc., constituted 1% or less of the total reaction mixture.

6. A. Farkas and H. W. Melville, *Experimental Methods in Gas Reactions*, Macmillan and Co., Ltd., London, 1939, p. 149.

At −112°C, in a similar experiment, it was observed that only about 96% of the reaction gases were condensable, indicating the presence of a gas or products volatile at that temperature. This suggested the presence of hydrogen bromide which has a vapor pressure of about 30 mm at that temperature, or some other gas volatile at −112°C. On the basis of the differences in volatility of bromine and hydrogen bromide, a group of experiments was performed where the reaction tube was equipped with a spiral trap and a metal valve for product separation.

By this method, unreacted Br_2 could be completely removed at −112°C and the more volatile product trapped at −196°C. Both gelatin and the material condensable at −196°C, identified as HBr, were analyzed for bromide content. Results are shown in Table I.

The experiments appeared to show that, for every bromine atom retained by the gelatin, there is formed a volatile gas containing an atom of the halogen. On the basis of these analyses, the reaction, within the limits of experimental error, appeared to be as follows:

$$Br_2 + \text{Gelatin} \rightarrow \text{Gel—Br} + \text{HBr}.$$

Since the calibration of the Pirani gauge was found to be proportional to $(M)^{-1/2}$ and the ratio of sensitivities of bromine to nitrogen had obeyed such a law, the experimental pressure increase found after reaction between bromine and gelatin may be attributed to the formation of hydrogen bromide. The Pirani gauge, on the basis of molecular weight, having a greater sensitivity for the hydrogen halide, would show an increase in pressure, on hydrogen bromide formation. A number of experiments were performed, generally in the same pressure range, and it was assumed that the pressure increase was due solely to the formation of hydrogen bromide. The rate of reaction was calculated on the basis of this assumption. These data are summarized in Table II.

Since plots of hydrogen bromide formation against reaction time as shown in Fig. 1 were linear over the range of reaction studied, it is believed that the initial reaction process is not characterized by an induction period.

Neither heating the gelatin sample overnight at 110°C, prior to evacuation, as shown by Experiments 2 and 6, nor varying the amount of gelatin affects the rate of reaction.

TABLE II — Rate of Reaction of Vacuum-Dried Gelatin with Bromine at Room Temperature

Experiment No.	Weight of gelatin (mg)	*P_0 (Br_2) (microns)	†P_f (microns)	P (HBr) (microns)	Time (min)	μg Br/min/gram of gelatin
1	9.2	7.07	7.11	0.04	5.5	2.5
2	10	6.86	6.95	0.09	16.0	1.8
6	10	7.93	8.04	0.11	19.0	1.9
7[a]	10	7.85	8.02	0.17	20.5	2.7
8	18.6	8.69	8.91	0.22	24.0	1.6, 2.2[b]
10[a]	18.6	8.63	8.80	0.17	18.0	1.7
14	18.8	4.88	4.95	0.07	20.0	0.5

* P_0 = initial pressure.
† P_f = final pressure.
[a] Experiments performed in presence of ultraviolet radiation.
[b] Bromide content of gelatin, analyzed by Analytical Chemical Dept., Eastman Kodak Co.

TABLE III — Effect of Temperature upon the Rate of Reaction of Bromine and Gelatin (31.5-mg samples)

Temp., °K	P_0(Br_2) (microns)	Time (min)	μgBr/min/gram of gelatin
274.6	8.08	60	1.6
298.1	8.70	30	2.2
312.5	7.85	25	3.3
339.3	8.32	15	5.1

The effect of bromine atoms on the rate of reaction was tested with two samples. The results shown in Table II revealed that, under the experimental conditions used, the presence of bromine atoms did not significantly alter the rate of reaction.

An experiment (No. 14 in Table II) at a lower initial concentration of bromine resulted in a reduction of the rate by about 30%. Further work would be required to determine whether a real fall-off in rate does occur at low initial pressures of bromine, since Experiment No. 18 (Table I) did not show this expected decrease in rate at the lower pressure.

For the determination of the variation of the rate of the reaction with temperature, experiments were performed at temperatures fom 1.5 to 66.2°C in a thermostated bath at initial pressures in the range 7–9 microns of bromine. The temperature-dependence of the reaction is shown in Table III. For each series of experiments, the logarithm of the relative rates of reaction was plotted against $1/T$. From the slope of the satisfactory Arrhenius plot, an activation energy of approximately 3.1 ± 0.6 kcal/mole was obtained from these experiments.

B. *Effect of Moisture on the Reaction*

Manometric studies of the effect of moisture upon the gelatin and bromine reaction were complicated by water-catalyzed attack of the halogen upon the stainless-steel surfaces. To better identify the role of moisture in the reaction, modified experiments were performed in which the halogen (7–9 microns) was added to gelatin samples, containing known quantities of moisture introduced by equilibrating samples over saturated salt solutions of given relative humidity. The samples were rapidly sealed off and permitted to react for 24 hours at room temperature. At the end of this period, all condensable gases were removed at −196°C and the gelatin was analyzed for bromide content. Controls were employed to determine the actual moisture content of the gelatin.

As a check on the preceding technique, similar experiments were performed at higher concentra-

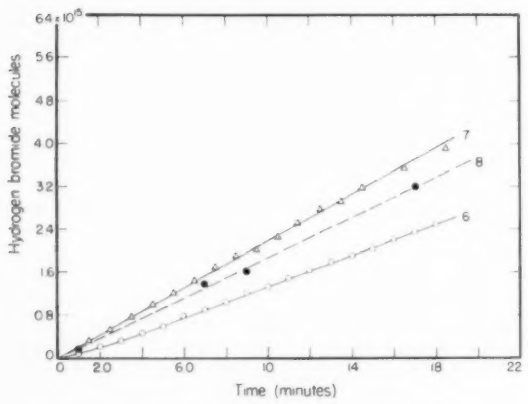

Fig. 1. The rate of formation of hydrogen bromide molecules as a function of time.

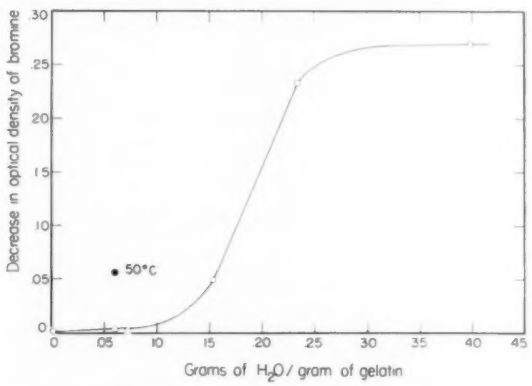

Fig. 2. The effect of moisture content upon the reaction between bromine and gelatin at room temperature: ○ — room temperature; ● — 50°C.

tions of bromine ($3.6 \times 10^{-3} M$) with carbon tetrachloride as solvent. Using a molar extinction coefficient of 205,[7] as found in this study, at 416 mμ, the wavelength of maximum absorption, the decrease in bromine concentration was measured by a Beckman DU Spectrophotometer. The results showing the dependence of the reaction upon moisture and the relatively good agreement for the two methods are shown in Table IV.

TABLE IV — Effect of Moisture upon the Reaction Between Gelatin and Bromine at Room Temperature

System	Weight of gelatin (mg)	% Moisture content of gelatin	μg Br reacted/gram gelatin
Br_2	200	0.0	17
$CCl_4 \cdot Br_2$	500	0.0	—
Br_2	20	6.5	93
$CCl_4 \cdot Br_2$	500	6.5	80
$CCl_4 \cdot Br_2$	500	7.0	96
Br_2	20	9.5	93

A plot of decrease in bromine density (original concentration $3.6 \times 10^{-3} M$) vs grams of water per gram of gelatin, Fig. 2, illustrates the accelerating effect of moisture upon the reaction. In calculating the amount of bromine disappeared, no correction was applied for the trace quantities which may have been consumed by hydrolysis, since control experiments with 23% and 38% water intentionally added to reaction concentrations of bromine resulted in decreases in bromine density of less than, and slightly more than, 1% at the low and high percentages mentioned. Thus evidence strongly suggests that water *per se* is not effective in decomposing molecular bromine in carbon tetracholoride, but it undoubtedly initiates and supports some type of ionic reaction between the protein and bromine.

Discussion of Results

Although the data are insufficient to give a detailed account of the reaction between gelatin and bromine, it is significant to note that the dry-state reaction is characterized by the slow evolution of a gas which has been identified as hydrogen bromide. The data, obtained by manometric and analytical techniques, suggest the formation of one mole of hydrogen bromide for every mole of bromine reacting.

The rate of reaction at room temperature is low, and does not possess an induction period. It has not been ascertained whether or not the presence of product molecules inhibits the reaction. Benson and Seehof,[8,9] in a vacuum study of the sorption of polar and nonpolar gases by proteins have shown that hydrogen chloride is irreversibly bound to the proteins, the amount held being intimately associated with the number of free amine groups available. In the present study, on the basis of the absence of free amine groups in the gelatin and the formation of such small quantities of hydrogen bromide, it does not seem probable that the gaseous product is able to attack the gelatin. Also the fact that a material balance was found tends to show that hydrogen bromide reaction with the gelatin is negligible.

The temperature coefficient of the reaction is suprisingly small; however, the reaction, over the temperature range studied, may vary, owing to changes in the accommodation coefficient of the halogen, diffusion effects, and changes in the structure of the protein molecule at the higher temperatures, such as breaking of hydrogen bonds.

The most probable site for reaction of the halogen with gelatin appears to be at a methylene group of the protein. The negligible amine content of the material strongly suggests that the amine group is of little importance as a possible source of reaction, and the breaking of the peptide linkage by molecular bromine, with simultaneous formation of hydrogen bromide, is not a likely process. However, Wood,[10] in a study of the action of bromogelatin and bromoimide compounds on sensitized emulsions, has found that gelatin (unspecified type) can be brominated to the extent of 12% by the action of molecular bromine contained in a solution of acetic acid and acetic anhydride. Analyses indicated that the bromogelatin consisted of 10.9% ionic bromine and the remaining 1.1% was assumed to be in the form of bromoimide groups, i.e., combined at the nitrogen of the polypeptide chain. The latter conclusion was based upon the comparative effectiveness of bromogelatin, along with N-bromoacetamide and N-bromosuccinimide, to desensitize emulsions. Since the systems employed by Wood contained water, the assumption that >N—Br bands are formed at the polypeptide group of the gelatin on this basis is questionable, for it is an established fact that bromoimides readily decompose in the presence of moisture.[11,12] The study, however, tends to substantiate the belief that gelatin is a bromine acceptor in a chemical sense.

Since the benzene ring reacts readily with chlorine or bromine in the presence of light by addition rather than substitution, and neither natural illumination nor strong ultraviolet irradiation altered the substitution reaction observed in this study, it is unlikely that aromatic chromophores, which are usually present as trace impurities in gelatin, play an important role in the reaction. Also, the fact that analyses showed that the amount of bromine picked up by the gelatin was essentially equal to, and certainly not greater than, that found in the volatile gas (Table I), further substantiates the belief that

7. A. I. Popov and E. H. Schmorr, *J. Am. Chem. Soc.*, **74:** 4672 (1952), reported a molar extinction coefficient of 208 for bromine in carbon tetrachloride.
8. S. W. Benson and J. M. Seehof, *J. Am. Chem. Soc.*, **73:** 5053 (1951).
9. ———, *ibid.*, **75:** 3925 (1953).
10. H. W. Wood, *Wissenschaftliche Photographie, Köln*, 1956, O. Helwich (ed.), Darmstadt, 1958, p. 212.
11. C. Djerassi, *Chem. Revs.*, **43:** 271 (1948).
12. A. Berka and J. Zyka, *Coll. Czech. Chem. Commun.*, **23:** 402 (1958).

addition of halogen to aromatic chromophores is of limited degree.

Since it is generally accepted that positive holes and electrons are liberated when energy is absorbed within silver halide crystals, and the trapping of the hole (bromine atom) and electron is very important for image formation, it was of interest to study the effect of bromine atoms on the halogen acceptance of gelatin. Irradiation of the bromine molecules in the region of the gelatin particles with wavelengths shorter than 630 mμ provided enough energy to cause dissociation from the 0 th level of the ground state. And since the maximum intensity of absorption occurs in the continuum, about 410 mμ, it is assumed that the unfiltered radiation produced a fairly large concentration of atoms which subsequently had little effect upon the reaction. Interference by protein absorption of incident energy and radical changes within the gelatin molecule due to photochemical effects probably did not occur, since the threshold for the photodecomposition of pure proteins is in the neighborhood of 300 mμ.[13] The use of Pyrex glass as the reaction system prevented heavy absorption in the region of protein decomposition.

The observation that bromine atoms had a negligible effect upon the rate of the reaction is not surprising, in view of the fact that reactions of bromine atoms with saturated compounds containing the carbon-hydrogen bond take place, if at all, only at relatively high temperatures.[14] The lower dissociation energy of the hydrogen-bromine bond in comparison with the dissociation energy of the carbon-hydrogen bond accounts for this. Also, instead of increased reactivity with gelatin in the presence of the atoms, the protein may serve as an efficient third body for bromine atom recombination.

The reactivity of gelatin for bromine is closely associated with the amount of water present and how this water is held by the gelatin. In Fig. 2, the S-shaped curve tends to rise at 10% moisture content, is linear in a limited range, and then saturates. If the water, held by gelatin at low moisture content, is considered "bound," or is so closely associated with the protein that it has lost its properties as a solvent, it may not be available for the bromine–gelatin reaction. Newsome and Sheppard,[15] in a study of adsorption and desorption of water vapor by gelatin sheet, observed that the rate of removal of water by evacuation at 25°C occurred readily at moisture levels above 8%, but extremely long hours (greater than 200) were required to reach a moisture content of 1%. This is indicative that, at low moisture levels, the molecules are strongly held by the protein. Bull[16] had discussed the adsorption on the basis of the Brunauer-Emmett-Teller theory.[17] The molecules adsorbed in the first layer of gelatin are considered to be strongly bound and water adsorbed in excess increases almost linearly with the water-vapor pressure. Pauling,[18] in an attempt to interpret Bull's data, considered the polar side chains of the amino acids in gelatin to be stronger bonding sites than C=O(NH) along the protein chain. He suggested that carbonyl groups are capable of binding water sufficiently strongly to be classed with the polar side-chain groups. This adsorption behavior of gelatin corresponds closely with the availability of water for initiating the reaction of the protein with bromine in carbon tetrachloride.

Figure 2 also reveals that, in the moisture region of 6% where the water molecules are strongly bound, a large increase in reaction could be accomplished by heating to 50°C. Undoubtedly, at this temperature a large number of bonds containing strongly adsorbed water molecules are broken and the molecules become available for hydrolyzing bromine, resulting in hypobromite attack on gelatin, a reaction which is more rapid than the molecular substitution process. In the presence of large concentrations of moisture, the apparent constancy of rate found in the study may be attributed to dilution of the reactive ion.

Of the ionic forms of bromine existing after hydrolysis, hypobromite appears to be more capable of reaction with gelatin than bromide, tribromide, or other ionic species. Grabar and Morel[19] have shown that reaction of gelatin with hypobromite destroys its gelling properties, and Davis[20] has observed that guanidino end groups, and possibly other side chains in the gelatin molecule, readily undergo hypobromite oxidation.

The products from the water-catalyzed bromine and gelatin reaction were not determined, and thus total bromine disappearance by hydrogen bromide or other volatile bromo-compound formation may be larger than is reported for the vacuum studies. In a recent study, Kelly[21] suggests the formation of hydrogen bromide on reacting bromine, produced *in situ* by the reaction of potassium bromate and potassium bromide with a gelatin solution. Since the pH of the reacting solution decreased rapidly, it was assumed that hydrogen bromide was produced through replacement of active hydrogen by a bromine atom.

Although such a product would corroborate the findings in the present dry-state reaction, it is noted that the rapid hydrolysis of bromine and the shift of equilibrium, resulting from hypobromite attack on gelatin, would likewise decrease the pH of the solution.

This study tends to show that, even in the dry state (in a chemical sense), the deaminated low-activity gelatin of relatively small surface area, within the limits of accuracy of the methods employed, is a sufficiently good halogen acceptor to combine with the order of (2-3) $\times 10^{-9}$ gram of bromine/mg of gelatin/min. According to Berg,[*] for low-intensity

13. H. Neurath and K. Bailey, *The Proteins*, Academic Press, Inc., New York, 1941, Vol. I, Part A, p. 447.
14. W. A. Noyes, Jr., and P. A. Leighton, *The Photochemistry of Gases*, Reinhold Publishing Corp., New York, 1941, p. 307.
15. P. T. Newsome and S. E. Sheppard, unpublished data.
16. H. B. Bull, *J. Am. Chem. Soc.*, **66:** 1499 (1944).
17. S. Brunauer, P. H. Emmett, and E. Teller, *ibid.*, **60:** 308 (1938).
18. L. Pauling, *ibid.*, **67:** 555 (1945).
19. P. Grabar and J. Morel, *Bull. Soc. Chem. Biol.*, **32:** 643 (1950).
20. P. T. Davis, *Nature*, **179:** 690 (1957).
21. W. D. Kelly, Jr., *J. Phot. Sci.*, **6:** 16 (1958).

exposures, at most 3.98×10^{-10} gram of halogen/sq cm are liberated. A typical photographic emulsion may contain as much as 1.32 mg of gelatin/sq cm, an amount which appears, on the basis of this study, to be quite capable of combining with the halogen liberated by a low-intensity exposure. The experiments also show that the efficiency of halogen removal by the protein is greatly enhanced in the presence of moisture.

Removal of halogen by gelatin may occur by various other mechanisms besides those mentioned. It has not been established but in the photographic process, even at low moisture content, water "bound" by gelatin may interact with the highly mobile positive hole at the surface of the grain, to initiate reaction of the complex gelatin–halogen–water system. It is evident that the existing experimental information on the halogen acceptance of gelatin is not adequate to provide a complete interpretation of this intricate reaction. Experiments over a wide range of halogen pressures, with variation of the surface area and constitution of the gelatin, and isolation plus identification of volatile products formed in the presence of moisture, would give valuable information leading to the ultimate elucidation of the mechanism of the bromine gelatin reaction.

Acknowledgments

The author is indebted to W. Vanselow and J. A. Leermakers for suggesting this problem and for their assistance. Thank are also extended to T. H. James, W. West, and M. L. Huggins for helpful discussions. Analyses of gelatin and gas samples by R. S. Miller, of the Analytical Chemistry Department, are gratefully acknowledged.

APPENDIX

In order to ensure a relatively reproducible and controllable history, the gelatin particles were weighed into sample tubes containing break seals. These samples were placed on the auxiliary portion of the vacuum system to be described later. Evacuation time at pressures of 10^{-6} mm of mercury or less was generally 30 hours or more, inasmuch as a 10-mg control, evacuated for that period of time at room temperature, exhibited a leak or desorption rate which approached that of the system alone. The leak rate may be described as an increase in pressure due to the desorption and diffusion of gases from the walls of the reaction system. Duplicate samples in weighing bottles were used to measure moisture content. Some samples were heated overnight at 100°C before evacuation.

Since bromine is a highly corrosive substance, the reaction system consisted of a Pyrex-glass reaction cell, equipped with one or more break seals, a platinum–iridium Pirani gauge and a Langmuir gauge. This system was isolated from the rest of the vacuum line by Veeco-type RSS stainless-steel 314 valves.[22] These valves contained Teflon gaskets. Excessive "flaming-out" of the system was avoided to prevent subsequent large adsorption of bromine by the valves. Bromine storage vessels were also isolated from the reaction vessel by these valves. The leak or degassing rate of the system was of the order of 1.5×10^{-6} mm of mercury/min after evacuation.

The remainder of the vacuum system consisted of a W. M. Welch Duo-Seal vacuum pump and a Distillation Products Industries GF-20 W oil-diffusion pump which produced a vacuum of less than 10^{-6} mm of mercury as measured with the McLeod gauge.

For measuring bromine pressures, a Langmuir gauge, capable of detecting 10^{-6} mm of mercury, was used. At the pressures employed in this study, the time required for damping of the gauge was too long for accurate measurements. Therefore, a platinum–iridium Pirani gauge, capable of measuring 10^{-3} mm of mercury, and giving instantaneous response, was constructed by A. Miller, of Distillation Products Industries. Although the zero of the Pirani gauge was found to vary on exposure to bromine, the appropriate correction could be applied by finding the actual pressure with the Langmuir gauge.

By using the McLeod gauge as a standard, the quartz-fiber and Pirani gauges were calibrated with dry nitrogen gas. Calibrations were taken over a period of months and the consistency of results indicated the reproducibility and stability of the gauges.

When the Langmuir gauge was compared with the Pirani for nitrogen and bromine gases, the calibration of the Pirani gauge was found to be proportional to $(M)^{-1/2}$, where M is the molecular weight of the gas in the gauge. This relationship is in agreement with that predicted by Yarwood and Le Croissette.[23]

From the reaction volume found gasometrically by use of dry nitrogen, a calibrated bulb and manometer, and assuming gas ideality, it was possible to calculate the number of atoms of bromine corresponding to one Pirani-gauge division. One scale division was found to correspond to approximately 1.86×10^{15} atoms of bromine or 9.3×10^{14} molecules.

A further check on the calibration, which was similar to that used by Luckey,[24] was provided by freezing a measured amount of bromine in a sample bulb which was then sealed off from the system. The bromine was kept at liquid-nitrogen temperature until the seal cooled, and the sample was then analyzed. The usual sample was approximately 40–90 μg, so that the results were subject to a possible error of about 2%. By this method an average of five analyses gave a value of about 1.90×10^{15} bromine atoms per scale division.

These data indicated that the Pirani-gauge calibration was not in serious error, and, taking into account the error of approximately 0.2 scale division in reading the gauge, it was estimated that 9.3×10^{14} molecules of bromine could be detected with an error of about 5%.

In some experiments, it was of interest to determine the effect of ultraviolet radiation upon the reaction of gelatin and bromine. For this purpose, a British Thomson-Houston ME/D 250-w high-intensity mercury source was employed. The light from this source was passed through a lens system and a heat filter (Aklo 396) to give a beam of 1.0 sq cm in area. The intensity of the source was not determined, but it was assumed to be of sufficient magnitude to dissociate the halogen.

In general, the following procedure was used in the experiments: After drying the gelatin by evacuation, the small volume sample tube, equipped with a break seal, was transferred to the known reaction volume and the

22. Manufactured by Vacuum-Electronic Engineering Co., New Hyde Park, Long Island, N. Y.

23. J. Yarwood and D. H. Le Croissette, *Vacuum*, **1**: 791 (1953).

24. G. W. Luckey, *J. Phys. Chem.*, **57**: 791 (1953).

system evacuated until a pressure of 10^{-6} mm of mercury or less was obtained. Next, the leak or desorption rate was measured, followed by the introduction of more than 12.0 microns of the halogen to "condition" the walls. After removal of this gas by evacuation, a quantity of bromine, which approximated that to be used for reaction with gelatin, was volatilized into the system and the subsequent leak or desorption rate, plus any wall interaction, was measured by the Pirani gauge.

The system was again evacuated and the reaction quantity of bromine was introduced. By use of a Pyrex-glass-covered metal bar, the break seal was broken, exposing the gelatin to the halogen. After reaction, the sample tube was removed from the system and the leak rate again measured. The leak rates were averaged and subtracted from the pressure changes accompanying the reaction. These leak rates closely paralleled the leak or desorption rates found with the halogen control.

The total gas production for a given reaction time was only 1–3% of the original concentration, but this production represented a consistent pressure increase above that of the leak or desorption rate. The leak or desorption rates measured prior to and after reaction generally agreed within less than 1%, so it is believed that the change represents a true pressure increase. No "dead-space" correction was made, since it would have resulted in only negligible changes in the pressures observed for the reaction.

In the study of the effect of water vapor on the reaction between gelatin and molecular bromine, the water stored in a bulb attached to the reaction system was degassed or deaerated at −112°C (*n*-propyl bromide and liquid nitrogen) before use to remove any entrapped air molecules. After "conditioning" the reaction walls with various quantities of the material, a given concentration of water molecules, measured by the Pirani gauge, was expanded into the reaction volume. The water vapor was condensed at −196°C on the gelatin sample and the tube, originally equipped with two break seals, was sealed off and the gelatin allowed to equilibrate with the vapor at room temperature for a period of twelve days to ensure equilibrium.[16] The sample was then caused to react with the bromine, which was introduced in the usual fashion.

Other gelatin samples were treated over saturated salt solutions in desiccators for twelve days or more, rapidly transferred to the vacuum system, and deaerated at −112°C. Given quantities of bromine were then condensed at −196°C into the sample tubes, sealed off, and permitted to interact with the gelatin for various periods of time at room temperature. The gelatin and condensable gases were analyzed for bromine content.

The experimental error of the gelatin analyses was approximately 20%, mainly owing to the small quantities of bromine involved (the order of 1 μg or less). Manometric measurements studied with the Pirani gauge gave reproducible results, but the experimental error of such a method was estimated to be between 20–25%.

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Photographic Developing Agents: 2. Quinones

R. W. HENN, J. F. TINKER, AND H. L. FIELDING, *Research Laboratories, Eastman Kodak Co., Rochester, N.Y.*

Strong developers are formed when many quinones are added to aqueous alkalies, either in the presence or absence of sulfite. In the absence of sulfite, the activity is probably due to a hydroquinone and possibly a hydroxyhydroquinone formed by the addition of the hydroxyl ion. The developer is less active in the presence of sulfite where the hydroquinone sulfonate is formed. Quinones with blocked *ortho*-positions do not form developers. A number of polyhydroxyanthraquinones were found to form developers but were less active than corresponding benzene and naphthalene derivatives.

The ability to form a quinone is characteristic of many photographic developing agents. Thus, hydroquinone may be oxidized by air or by silver bromide to quinone, *p*-aminophenol to quinonimine, etc. The chemistry of the actual oxidation is complex and proceeds through various intermediate compounds, including semiquinones and possibly peroxides, free radicals, and hydroxyhydroquinone.[1-3] Also, the end product need not be quinone but can be a condensation product of the humic acid type or a hydroquinone sulfonic acid.[1] The photographic developer, therefore, unlike the quinhydrone electrode, does not represent a reversible system.[4]

Hydroquinone, aminophenol, or phenylenediamine, speaking generically in each case, is commonly and accurately considered the developing agent and the quinone is the oxidation product. However, Rao and Pandalai reported in 1933 that a solution of quinone in sodium sulfite would develop a photographic plate.[5] This might be explained on the basis of reduction of the quinone by the sulfite or even by alkalies as indicated in Refs. 1–4, but the results of actual experiments were not reported. It seems therefore worth while to report certain of our observations concerning the developing properties of solutions of quinones. These observations show correlations with structure, while the rate measurements in the presence and absence of sulfite point to the formation of at least two different developing agents.

Experimental Observations

1. *Developing Properties of Various Quinones*

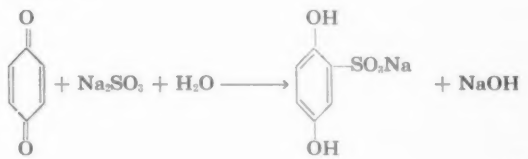
Approximately thirty quinones were tested for developing properties, using the spot-test technique described previously[6] and reviewed in the section on *Experimental Procedures*. The data obtained with the quinones are presented in Tables I–III, and may be compared with those obtained with conventional developing agents, presented in Table IV.

1,4-Benzoquinone ("quinone") and most of its mono- and disubstituted derivatives yielded active developers in this caustic sulfite solution. 1,4-Naphthoquinone, 1,2-naphthoquinone, juglone (5-hydroxy-1,4-naphthoquinone), and 5,8-dihydro-1,4-naphthoquinone also yielded active developers. Significantly, solutions of the tetrasubstituted benzoquinones, chloranil and chloranilic acid, failed to produce an image as did the 2,3-dichloronaphthoquinone, anthraquinone, or phenanthraquinone. Anthraquinone-1-sulfonic acid and anthraquinone-2-sulfonic acid, 2-aminoanthraquinone, and 2-methyl-1-nitroanthraquinone also failed to develop.

The polyhydroxy anthraquinones, alizarin (dihydroxy), rufigallol (trihydroxy), and anthragallol (hexahydroxy) solutions developed, but for a different reason. The compounds are analogs of catechol and pyrogallol and should be capable of further oxidation. They are weaker developers than the benzene and naphthalene derivatives given in Table IV, and sulfonation destroyed the remaining activity, whereas hydroquinone sulfonic acid still develops vigorously under these conditions.

2. *The Effect of Sulfite*

The data just given could be explained by predicting reductive sulfonation to the hydroquinone, typically:



(1)

Communication No. 2060 from the Kodak Research Laboratories, presented at the National Conference, Chicago, 30 October 1959. Received 23 October 1959.

1. C. E. K. Mees, *The Theory of the Photographic Process*, rev. ed., The Macmillan Co., New York, 1954, p. 506 ff. (Includes extensive bibliography.)
2. T. H. James, *J. Phot. Soc. Am.*, **10:** 271 (1944).
3. J. E. LuValle and W. Goldberg, *J. Phot. Sci.*, **6:** 176 (1958).
4. A. E. Cameron, *J. Phys. Chem.*, **42:** 1217 (1938).
5. G. G. Rao and M. Pandalai, *Nature*, **131:** 100 (1933).
6. R. W. Henn and Sue V. Carpenter, *Phot. Sci. and Eng.*, **3:** 139 (1959).

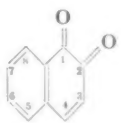
TABLE I — Development by 1,4-Benzoquinones
(In the presence of Na_2SO_3+NaOH) — Kodak Velox Paper

Number	Compound	Substituents 2	3	5	6	Development Image	Fog
I	1,4-Benzoquinone	H	H	H	H	+++	+
II	Toluquinone	CH_3	H	H	H	+++	+
III	Sulfophenylquinone	p-$C_6H_4SO_3H$	H	H	H	++	+
IV	Xyloquinone	CH_3	H	CH_3	H	++	+
V	Dichloroquinone	Cl	H	Cl	H	+++	+
VI	Toluquinonemonosulfonate	SO_3H	H	CH_3	H	+++	+
VII	Thymoquinone	CH_3	H	C_3H_7	H	+++	++
VIII	Dihydroxyquinone	OH	H	OH	H	0	0
IX	Chloranilic acid	OH	Cl	OH	Cl	0	0
X	Chloranil	Cl	Cl	Cl	Cl	0	0

TABLE II — Development by Naphthoquinones
(In the presence of Na_2SO_3+NaOH) — Kodak Velox Paper

Number	Compound	Substituents 2	3	5	8	Development Image	Fog
XI	1,4-Naphthoquinone	H	H	H	H	+++	++
XII	Juglone	H	H	OH	H	+	tr
XIII	Dihydronaphthoquinone	H	H	H_2	H_2	+++	++
XIV	Dichloronaphthoquinone	Cl	Cl	H	H	0	0
XV	1,2-Naphthoquinone					+++	+

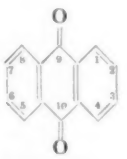
XI–XIV



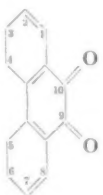
XV

TABLE III — Development by Anthraquinones and Phenanthraquinone
(In the presence of Na_2SO_3+NaOH) — Kodak Velox Paper

Number	Compound	Substituents 1	2	3	4	5	6	7	Development Image	Fog
XVI	Anthraquinone	H	H	H	H	H	H	H	0	0
XVII	Alizarin	OH	OH	H	H	H	H	H	++	+
XVIII	Anthragallol	OH	OH	OH	H	H	H	H	++	+
XIX	Rufigallol	OH	OH	OH	H	OH	OH	OH	+	tr+
XX	Alizarin Red S	OH	OH	SO_3H	H	H	H	H	0	0
XXI	Quinizarin-5-sulfonate	OH	H	H	OH	SO_3H	H	H	0	0
XXII	Phenanthraquinone	H	H	H	H	H	H	H	0	0



XVI–XXI



XXII

However, that this is not the only possible reaction was demonstrated by repeating certain of the spot tests in the absence of sulfite. This comparison showed the following degrees of image formation:

	NaOH Only	NaOH + Na_2SO_3
1,4-Benzoquinone	+++	+++
1,4-Naphthoquinone	+++	+++
1,2-Naphthoquinone	+	++

The presence of sodium sulfite is clearly not a requisite for development.

Next, the relative developing rates were measured in the presence and absence of sulfite. These measurements employed James's[7] air-free equipment, in which separate solutions of the quinone in acid, and of the alkali, were swept with nitrogen and then combined. Nitrogen also provided vigorous agitation during development. Two buffer systems were used: (a) acetic acid and sodium carbonate at a pH of 10, and (b) phosphoric acid and sodium hydroxide at a pH of 11.5, using quantities predetermined to achieve the desired pH.

7. T. H. James, *J. Phys. Chem.*, **43:** 701 (1939).

TABLE IV — Development by Phenolic Agents
(In the presence of Na_2SO_3+NaOH) — Kodak Velox Paper

Number	Compound	Image	Fog
XXIII	Hydroquinone	+++	++
XXIV	Hydroquinonemonosulfonate	+++	+
XXV	Catechol	+++	++
XXVI	Pyrogallol	+++	++
XXVII	1,4-Dihydroxynaphthalene	+++	++
XXVIII	1,5-Dihydroxynaphthalene	+++	++
XXIX	Quinhydrone	+++	+

TABLE V — Presence vs Absence of Sulfite
Kodak Fine Grain Positive Film — Nitrogen-Burst Equipment

Agent	Alkali	Sulfite	pH	Time (min.)	Image Density 3rd Step	Image Density 9th Step	Image Density Fog
1,4-Benzoquinone	Na_2CO_3	Yes	10.0	22.4	2.00	0.69	0.30
1,4-Benzoquinone	Na_2CO_3	No	10.0	4.7	2.00	0.66	0.32
1,4-Benzoquinone	Na_3PO_4	Yes	11.6	3.3	2.00	0.67	0.16
1,4-Benzoquinone	Na_3PO_4	No	11.5	1.5	2.00	0.47	0.14
1,4-Naphthoquinone	Na_2CO_3	Yes	10.0	1.1	2.00	0.91	0.48
1,4-Naphthoquinone	Na_2CO_3	No*	10.0	20.0	2.00	1.78	1.60
Hydroquinonemonosulfonate	Na_2CO_3	Yes	10.0	39.8	2.00	0.42	0.11
Hydroquinonemonosulfonate	Na_2CO_3	No	10.0	30.9	2.00	0.22	0.04

* Very little dissolved.

TABLE VI — Effect of Order of Mixing
Kodak Fine Grain Positive Film — Processing on Sensitometric Developing Wheel

Procedure	Mixing Order 1	2	3	pH	Time (min)	Image Density 3rd Step	Image Density 9th Step	Image Density Fog
(a)	Quinone	Na_2SO_3	Na_2CO_3	10.0	64.0	0.18	0.04	0.02
(c)	Na_2SO_3	Na_2CO_3	Quinone	10.0	57.5	2.00	0.58	0.10
(b)	Quinone	Na_2CO_3	Na_2SO_3	10.0	31.6	2.00	0.84	0.39
(b)	Quinone	Na_2CO_3	Na_2SO_3	10.0	12.0	0.36	0.23	0.18
(a)	Quinone	Na_2SO_3	Na_3PO_4	11.8	35.1	2.00	0.72	0.21
(c)	Na_2SO_3	Na_3PO_4	Quinone	11.8	13.5	2.00	0.92	0.19
(b)	Quinone	Na_3PO_4	Na_2SO_3	11.8	9.1	2.00	0.99	0.27
(c)	Na_2SO_3	Na_2CO_3	$HqSO_3Na$*	10.0	64.0	0.16	0.06	0.02
(c)	Na_2SO_3	Na_2CO_3	$HqSO_3Na$	10.0	175.0†	2.00†	——	0.13†
(c)	Na_2SO_3	Na_3PO_4	$HqSO_3Na$	11.5	27.0	2.00	0.99	0.17
(c)	Na_2SO_3	Na_2CO_3	Hydroquinone	10.0	12.8	2.00	0.72	0.10
(c)	Na_2SO_3	Na_2CO_3	Hydroquinone	11.5	3.6	2.00	0.77	0.13

* Sodium hydroquinone monosulfonate † Extrapolated curve

Specially purified samples of 1,4-benzoquinone and 1,4-naphthoquinone were employed. Sodium hydroquinone monosulfonate was included as a control. In each case, the solution was 0.02 molar with respect to developing agent, 0.2 molar with respect to buffer, and 0.2 molar with respect to sulfite, where employed. The quinone was dissolved in the acid, while the alkali and sodium sulfite were mixed together, and the two solutions were combined after freeing them from oxygen. Kodak Fine Grain Positive Film was employed for the rate measurements.

The data of Table V, and Figs. 1–4, show that the benzoquinone was a much more active developer in the absence of sulfite than in its presence and de-

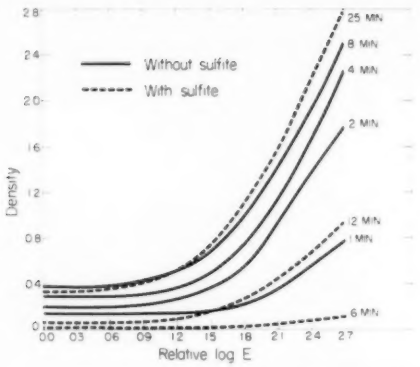


Fig. 1. Characteristic curves obtained by developing Kodak Fine Grain Positive Film with benzoquinone at pH = 10.0: In the absence of sulfite ——; in the presence of sulfite – – –.

veloped in about one-fifth the time at pH 10 and one-half the time at pH 11.5. However, even in the presence of the sulfite, the quinone was rather more active than the hydroquinone sulfonate. The data obtained with the naphthoquinone are less meaningful since its solubility was very low in the absence of sulfite, reducing its effective concentration. The mixed solutions were very dark in the absence of sulfite and light yellow in its presence.

3. *Effect of Order of Mixing*

The solutions employed in these experiments also contained 0.02 molar concentrations of the developing agent and 0.2 molar concentrations of sodium sulfite and the carbonate or phosphate alkalies. Activity was again assayed with Kodak Fine Grain

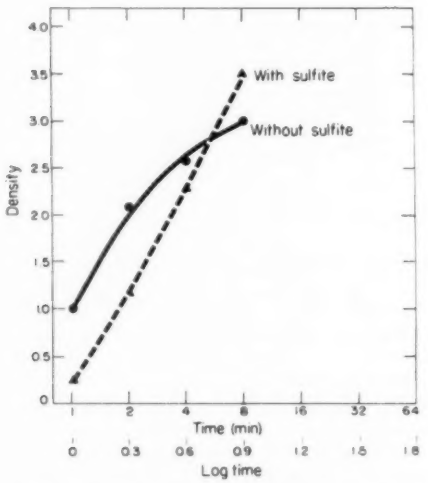


Fig. 3. Activity of benzoquinone developer at pH = 11.5, using sodium phosphate as the alkali: Without sulfite——; with sulfite – – –.

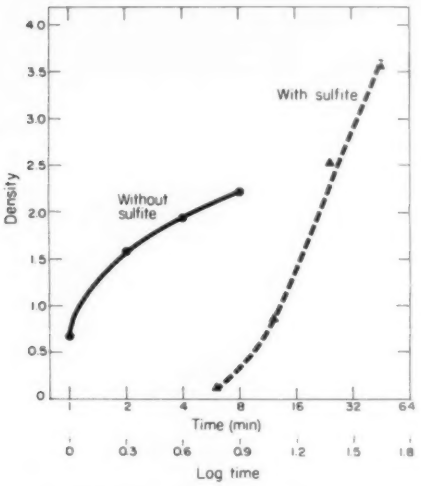


Fig. 2. Activity of benzoquinone developers in terms of image density (of the 3rd exposure step) vs. time: Without sulfite ——; with sulfite – – –. pH = 10.0, sodium carbonate as the alkali.

Positive Film, but the small-scale sensitometric processor of Henn and Hughes[8] was employed because of the small quantities of chemicals required. These experiments were designed to allow (a) brief reaction of the quinone with the sulfite before the alkali was added, (b) brief reaction of the quinone with the alkali before the sulfite was added, and (c) competitive reaction of the type common to the preceding experiments, by adding the quinone directly

8. R. W. Henn and K. R. Hughes, *Phot. Sci. and Eng.*, **2**: 81 (1958).

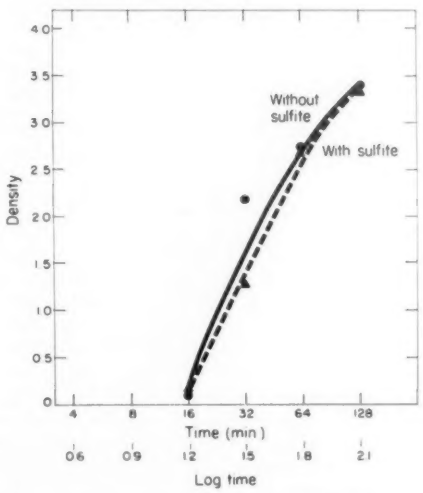


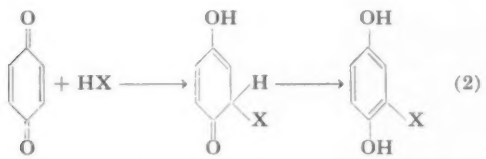
Fig. 4. Development by hydroquinone sulfonic acid at pH = 10.0: Without sulfite——; with sulfite – – –.

to the alkali–sulfite mixture. After completing the mixing procedure, which required only a few minutes, the pH was adjusted and the solutions were allowed to stand one hour before processing. A green-colored solution resulted from the first and third procedures, but mixing the quinone first with the sulfite yielded a red solution.

These procedures produced developers of greatly varying activity. Initial reaction with alkali gave developers which were four or five times as active as those prepared when the quinone was initially reacted with the sulfite (Table VI). Addition to the mixture of sulfite and alkali produced developers of intermediate activity. The activity of the developers produced by initial reaction with sulfite was close to that of the hydroquinone monosulfonate. The most active developers, obtained by mixing the quinone first with the alkali, were still only about 40 per cent as active as the hydroquinone developer at the same pH. Further change occurred on longer standing, and the developer mixed by procedure (b) produced only one-half the image density after 6 hours and one-ninth the image density after standing 24 hours in a stoppered flask.

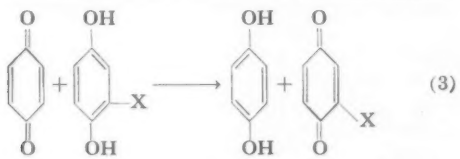
Discussion

A reasonable explanation for the developing activity of the quinone solutions is obtained by a review of their 1,3-addition reactions. These are discussed by Allen and Blatt.[9] Initial addition proceeds in two steps.

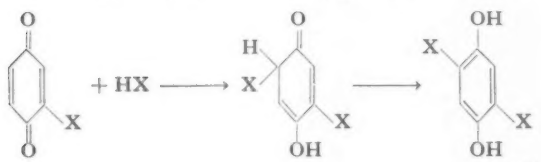


(2)

It is not unusual for this reaction to proceed further.



(3)



(4)

In the case of the reactions involved in these experiments, X may be the SO_3H^- ion, or alternately, the OH^- ion. Where the sulfite ion is the nucleophilic agent, Eq. (2) becomes Eq. (1) and hydroquinone monosulfonate is formed. When no sulfite is present, X must be the hydroxyl ion and the product will be hydroxyhydroquinone by Eq. (2) or hydroquinone and hydroxyquinone by Eq. (3).

The experimental data may now be examined in terms of these reactions. Where the quinone was first mixed with the sulfite, the hydroquinone sulfonate seems to have been formed nearly quantitatively, as indicated by the similar activity of these developers and the developers containing hydroquinone monosulfonate (Table VI). But where the quinone first reacted with the alkali (hydroxyl ion), the developer was more active, because of the formation of hydroxyhydroquinone, hydroquinone, or some mixture. Hydroxyhydroquinone is formed more directly as in Eq. (2) and LuValle considers it to have an important role in quinone chemistry. However, on the basis of the literature and sensitometric data, it does not seem to be a likely end product, especially since hydroxyhydroquinone has about three times the activity of hydroquinone at a pH of 10 and produces high fog. On the other hand, the developers produced when the quinone first reacted with the alkali had about 40 per cent of the activity of the 0.02 molar hydroquinone and did not produce high fog. This is not far, however, from the activity that would be anticipated for the 0.01 molar hydroquinone, which would be formed by Reaction (3), and therefore favors the domination of this reaction.

When the quinone is added to a mixture of sulfite and alkali, the sulfonation and hyroxylation reactions compete, and, indeed, the developers have intermediate activity. Probably sulfonation reaction dominates because sulfite is both the stronger nucleophilic agent and present in the greater concentration. However, relatively low proportions of the more active hydroquinone would have considerable sensitometric effect.

Support for the formation of hydroquinone by alkaline solutions of quinone is found in the literature. Scheid[10] held an alkaline solution of quinone at 100°C for 6 hours and found it completely changed to hydroquinone and quinhydrone. Hesse[11] found quinone crystals to disappear from an aqueous sodium acetate solution and quinhydrone and hydroquinone to be formed, later changing to a hydroquinone acetate. Cameron[4] and James[2] consider the reaction a disproportionation.

$$2\ C_6H_4O_2 + H_2O \rightarrow C_6H_4(OH)_2 + C_6H_3(OH)O_2 \qquad (5)$$

This reaction produces the same end result as a summation of Eqs. (2) and (3).

Cameron also reports a further step corresponding to Eq. (5).

$$2\ C_6H_3(OH)O_2 + H_2O \rightarrow C_6H_2(OH)_2O_2 + C_6H_3(OH)_3 \qquad (6)$$

The sulfonation reaction is well known photo-

9. C. F. H. Allen and A. H. Blatt, in *Organic Chemistry*, H. Gilman (ed.), J. Wiley and Sons, Inc., New York, 1938, Vol. I, Chap. 6, p. 600.

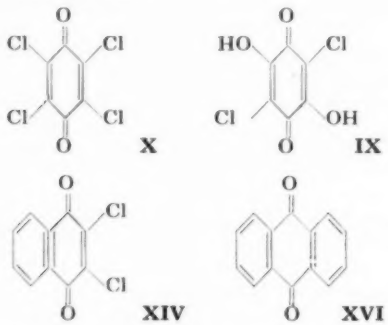
10. B. Scheid, *Ann. Chem.*, **218:** 195 (1883).
11. O. Hesse, *Ann. Chem.*, **220:** 365 (1883).

graphically and need not be discussed. Mees[1] gives a number of literature references.

The possibility of some other mechanism than reduction to a hydroquinone is not completely excluded since quinone can be oxidized further to humic acids of the formula $(C_6H_4O_3)_x$ (Ref. 1) or the peroxides $K_2C_6O_6$ and KHC_6O_6, reported by Astre.[12] However, even in these cases, initial reductive addition of hydroxyl ions seems likely, while a peroxide seems an improbable end product of development.

Structural Influences

The addition-reduction reactions mentioned are not limited to 1,4-benzoquinone but should occur with any quinone containing a free hydrogen in a suitable position for a 1,3-addition reaction to occur. This is supported by the literature; for example, 2-hydroxy-1,4-naphthoquinone is obtained as a product of the aerial oxidation of 1,4-naphthoquinone, and juglone (**XII**) is oxidized to 2,8-dihydroxynaphthoquinone. All but one of the quinones of Tables I–III which fit this requirement (that is, have a free hydrogen *meta* to the C=O group) have formed developers, but chloranil (**X**), chloranilic acid (**IX**), dichloronaphthoquinone (**XIV**), and anthraquinone (**XVI**), do not have the required free hydrogen atom and do not form developers.



Phenanthraquinone fails to develop for the same reason. The failure of the 2,5-dihydroxy-1,4-benzoquinone (**VIII**) to develop appears anomalous since it fits the 1,3-addition rule, and it is also a hydroquinone and nominally capable of further oxidation. However, in practice, this is not true. As a hydroquinone, it has no oxidation product and is, indeed, easily prepared by extensive oxidation of hydroquinone in mildy alkaline solution. Cameron also obtained the dihydroxyquinone as an end product (Eq. (6)) and found no evidence that it could undergo further addition reactions. However, the dihydroxyquinone can be reduced by stronger agents, such as zinc and hydrochloric acid. When this was done, the resulting solution was found to develop actively, an image being obtained even at a pH of 7.0. The active developer is presumably 1,2,4,5-tetrahydroxybenzene.

12. C. Astre, *Compt. rend.*, **121**: 559 (1895).

Experimental Procedures

Chemicals Employed

The quinones and developing agents of Tables I-IV are typically commercial chemicals obtained in the purest grade available, commonly White-Label Eastman Organic Chemicals, although others were specially synthesized. The data of Figs. 1–4 and Tables V and VI were obtained with highly purified materials.

The 1,4-benzoquinone was recrystallized three times from boiling ligroin (bp, 100°–110°C). From 20 grams of quinone in 240 ml of ligroin the yield was 11.6 grams, mp, 111°–113°C. Twenty grams of the 1,4-naphthoquinone was dissolved in ether, treated with decolorizing charcoal, and evaporated until crystals began to form. The solid was collected and washed. The mother liquor was treated with carbon black in the same manner twice more. All the crystals were recrystallized once more. Yield: 12.3 grams, mp, 123°–125°C.

Spot Tests

The procedure used in spot-testing for developing activity was described in the preceding paper. One hundred milligrams of the quinone were dissolved in 2 ml of acetonitrile and added to 8 ml of a solution containing 250 mg of sodium hydroxide, and 250 mg of sodium sulfite. This was spotted onto Kodak Velox F-4 Paper for 3 min at about 75°F, and the degree of development rated from "tr" (trace) to "+++" (maximum black).

Developing-Rate Tests, Nitrogen Equipment

The equipment and procedure have already been described. A typical developer comprised: Part A, Benzoquinone, 0.006 mole; phosphoric acid, 0.06 mole; water to 200 ml. Part B, Sodium hydroxide, 0.17 mole; sodium sulfite (optional), 0.06 mole; water to 100 ml. The volume after combination was 300 ml, and the pH was 11.48, requiring no adjustment. In other variations, (a) the sulfite was omitted; (b) sodium carbonate and acetic acid were substituted for the sodium hydroxide and phosphoric acid; (c) the quinone was replaced by naphthoquinone or sodium hydroquinonemonosulfonate; and (d) the pH was adjusted with acetic acid or with sodium hydroxide. Data were gathered for Kodak Fine Grain Positive Film, and development was at 68°F.

Developing-Rate Tests, with the Sensitometric Processing Wheel

The solutions contained 0.02 mole of the developing agent, 0.2 mole of sodium carbonate or phosphate, and 0.2 mole of sodium sulfite per liter. The pH values were adjusted to the specified values by the addition of acetic acid, employing suitable glass and calomel electrodes. Kodak Fine Grain Positive Film used for the measurements was developed at 68°F.

Sensitometric Data

The film was exposed behind a step wedge and cut into strips before development. The density of the third step, selected for the primary measurements, lies high on the straight-line portion of the characteristic curve (see Fig. 1), while the ninth step received 0.9 log E unit less exposure. Under these exposure conditions, a third step density of 2.0 approximates the degree of development recommended for this product.

PHOTOGRAPHIC SCIENCE AND ENGINEERING
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An Approach to Monobath Kinetics

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Monobaths are formulated by empirically adjusting the chemical constituents. If the kinetics of the process were known, this empirical approach could be augmented. A mathematical equation is presented which represents the kinetic behavior of monobaths. Experiments designed and carried out by the authors substantiate the kinetic relationship.

A. A. Newman's excellent critical survey[1] of 70 years of monobath progress decries the lack of theoretical papers in the field. This in part is due to the lack of understanding of the basic chemistry and kinetic behavior involved in combined developing and fixing solutions. Since monobath processing goes to completion, little is known of the rate at which image density grows, or the parameters which affect this growth.

This suggests a definite need for an investigation of monobath kinetics which might reveal certain invariant processing characteristics. If the kinetic behavior were known, the empirical approach to monobaths might be augmented. Further, through the kinetics, it might be possible to get to the fundamental reactions of the process and thereby establish first principles from which relationships having greater theoretical significance could be established.

It is the purpose of this paper to offer a provisional kinetic equation generally applicable to monobaths and provide some verifying experimental evidence.

Basic Requirements

Certain basic requirements for a mathematical description of the monobath process must first be established. These will hinge on the known chemical behavior of certain of the monobath constituents. Further, a few simplifying assumptions will be introduced in order to keep the mathematics reasonably uncomplicated.

(1) There must be a negligible development induction period. This can be accomplished by synergistic developing agents.

(2) There must be a large initial rate of development.

(3) The fixation induction period must be such that fixing activity is not immediately effective.

Because of these three separate effects, a representative mathematical curve must be concave downward, will have a steep initial rise, and will begin effectively at the origin of coordinates.

(4) As processing time increases, image growth is slowed by the now competing reactions for the available silver halide. As a result of this, the curve should become less steep in its rise.

(5) At some finite time (denoted as t_f) image growth should cease.[2] There will be some gamma* reached at this time (denoted as γ_f).

These considerations can be embodied in a general functional equation from which several kinetic expressions may arise.

$$d\gamma/dt = K(\gamma_f - \gamma)f(t, t - t_f) \qquad (1)$$

The Kinetic Equation

The functional relationship of Eq. (1) guided the early experiments. The results of these experiments, together with the remaining basic requirements, prescribed the following equation for representing the growth of gamma with processing time:

$$\gamma = \gamma_f\left[1 - e^{-\beta(t/[t_f - t])^a}\right] \qquad (2)$$

$$0 \leq t \leq t_f$$

where

t_f = time at which image growth ceases
γ_f = gamma obtained in time t_f
β = velocity constant of processing
a = constant
t = time at a given stage of processing
γ = gamma reached at some time, t

The values of the constants may vary with temperature. Temperature variations are not included in the mathematical description, but must be adduced experimentally.

There are other equations which could meet the basic requirements, but none has been found in such a compact form.† Since this possibility exists, how-

Presented at the National Conference, Chicago, 29 October 1959. Received 28 August 1959; revised 10 March 1960.

1. A. A. Newman, *Brit. Phot.*, **23**: 30 (Jan. 1959).

* In photographic kinetics, it has generally been established that gamma and density follow the same law of growth. Only gamma is used as the dependent variable throughout this paper, for reasons of experimental convenience.

† A minimum number of constant terms has been used and all but one (a) reasonably justified, either from elementary kinetic considerations or from the known behavior of monobath solutions.

2. R. G. Clarke *et al.*, *Phot. Eng.*, **4**: 231 (1953).

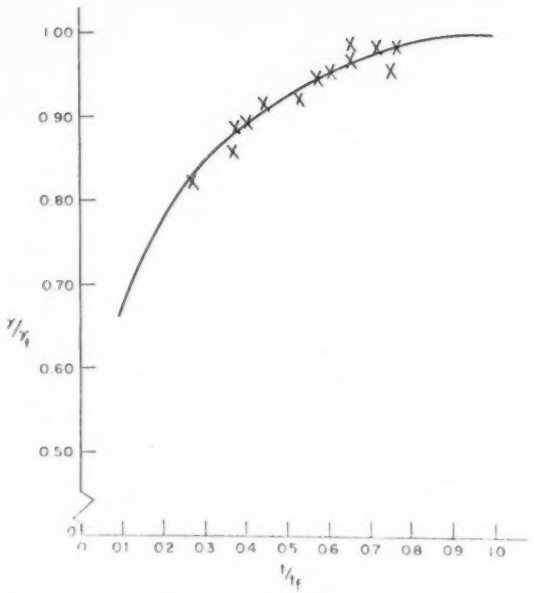

Fig. 1. Representative kinetic behavior for Panatomic-X 35mm film and Boston University Monobath No. 438 at 20°C. X's = experimental points; —— = kinetic equation. The constant terms for kinetics are determined by mathematical analysis and the equation plotted. The values of the constants for the above conditions are listed in Table I. Experimental points are shown to indicate (1) the degree of fit, and (2) the region of experimental sensitivity.

ever, Eq. (2) is merely a statement of mathematical sufficiency.

Experimental Considerations

General Discussion

Experimental data were not available in the literature to test the sufficiency of the kinetic equation. Therefore, a general method of experimentation was designed to provide the necessary information.

In order to ascertain the increase of gamma with processing time, the growth of the image must be experimentally halted, but fixation allowed to proceed. Such an operation is impossible with a monobath alone; rinsing in an acid stop bath and subsequent acid fixation achieves this effect at the proper point in time. Since accurate data of high precision are required, it is necessary to standardize procedures to minimize experimental error. To this end, special consideration should be given to processing equipment which provides constant agitation and maintains constant temperature during the course of the processing.

Apparatus

A processing device was designed and constructed which met the necessary requirements for agitation and temperature. A sensitometric strip was fastened to the outside of a drum rotating at 6 rpm and placed in a tank containing the monobath. The monobath was agitated by nitrogen bubbles constantly emanating from a ring of holes located at the bottom of the tank. These holes were located so that the rising bubbles would not touch the film strip. Gas flow was controlled through a differential manometer.

Sensitometric strips were exposed in an Eastman Intensity Scale Sensitometer, Special Type 1B. The diffuse density of processed strips was measured with a Model 12 Ansco-Macbeth Densitometer.

Experimental Procedure

Under controlled conditions of agitation and temperature, monobath kinetics were investigated. Arbitrarily, Panatomic-X 35mm film and Boston University Monobath No. 438[3] were chosen for this study. Three sets of sensitometric strips were processed at a given temperature. A control set consisting of three strips was processed for 5 min in monobath only. The second set of three strips was processed in monobath for 2 min, acid stop for 30 sec, and acid fixing bath for 2 min. These strips provided values of γ_f. The third set of strips furnished gamma values between zero and γ_f. Strips of this set were processed for times varying from approximately 10 sec to 1 min in the monobath, 30 sec in the acid stop, and 2 min in the acid fix. Limitations inherent in the experimental apparatus lowered data reliability for monobath processing times below 10 sec. Values of γ/γ_f versus processing time were thus obtained, and the three remaining kinetic constants (a, β, and t_f) determined by a least squares method.*

TABLE I

Summary of Kinetic Constants for Panatomic-X 35mm Film and Boston University Monobath No. 438

	Temperature	a	β	t_f	γ_f
	20°C	0.382	2.58	55.0	0.97
	25°C	0.410	2.60	40.0	0.97
	30°C	0.600	2.68	35.0	0.97
Variation...	20–30°C	+57%	+4%	−36%	——

Experimental Results

Experiments were carried out at 20°, 25°, and 30°C. The kinetic constants were computed for each temperature and are shown in Table I. The kinetic equation at 20°C is plotted in Fig. 1, and is representative of behavior at the other temperatures.

* Equation (2) is an equation which is termed "nonlinear in the constant terms." Such an equation cannot be fitted by the usual linear methods. A systematic procedure was established, the basic outline of which can be found in Deming's *Statistical Adjustment of Data* (Wiley, New York, 1938), which not only determined the constant terms but established a measure of correlation between curve and data.

3. Harry S. Keelan, *J. Phot. Sci.*, **5**: 144 (1957).

The average correlation coefficient* for these experiments was 0.980.

Discussion

Examination of Table I reveals that, over the range of temperatures considered, γ_f and β exhibit negligible variation. These appear to be invariant processing characteristics which are independent of the kinetics.

The remaining two constants, a, and t_f, show definite variation with temperature. The physical quantity, t_f, which decreases with temperature, measures the time for full image growth. Since development and fixing activities increase with temperature, γ_f will effectively be reached in a shorter time. Although a is primarily a constant of adjustment, its striking variation with temperature suggests a more fundamental chemical meaning. This can be established only by additional experimentation.

Conclusions

A kinetic equation representative of combined developing and fixing solutions has been devised and experimentally substantiated for Panatomic-X 35mm film and Boston University Monobath No. 438. Further experimentation will be necessary to fully establish and extend these kinetic studies. It is felt that while the monobath kinetic equation and experimental results are only preliminary, this new approach should stimulate interest toward further basic research in this area.

* A correlation coefficient measures agreement of mathematical function and experimental data. When there is no correlation, the value of this coefficient is zero; complete agreement is indicated by a value of 1.

Acknowledgments

Acknowledgment is gratefully made to Harry S. Keelan, who first made the authors aware of the problem and maintained a continuing active interest though no longer associated with the project. The authors further wish to express their gratitude to the research staff of the Itek Corporation in support of these investigations, and to thank, in particular, William M. Drumm for technical assistance in the areas of sensitometry and densitometry; Henry T. Sproul, who aided in the design and construction of the special processing equipment; Eileen T. Ahern and Richard A. Read, who assisted with the mathematical computations; and Richard B. Oliver and Joseph P. Vrabel for special assistance.

• Notes from the Editor

Discussion and Evaluation — A New Section

The paper by Dr. Bemiss in this issue initiates a section on *Discussion and Evaluation* which we hope to continue in future issues of *P S & E* as suitable material becomes available. We should welcome for this section submission of short papers concerned with *retrospection* (past performance analysis), *cogitation* (thoughts for present consideration), or *prognostication*, all, of course, within the scope of photographic science and engineering.

Conference on Ultimate Sensitivity in Photography

The Scientific & Technical Group of the Royal Photographic Society of Great Britain plans to hold a conference on "The Ultimate Sensitivity in Photography—Today and Tomorrow" in London in December 1960. The following is a list of headings under which contributions would be welcome:

1. Sensitized materials: sensitization techniques, grain size, layer structure, and exposure physics
2. Hypersensitization
3. Optics: design of focused and nonfocused systems
4. Latent image intensification
5. Processing
6. Developed image structure
7. Intensification
8. Theoretical considerations: quantum efficiency; information theory
9. Speed evaluation for maximum speed materials

Contributions must be directly relevant to the question of maximum sensitivity in existing or speculative photographic systems. Papers will be presented in English; the Committee will provide readers for papers by authors who cannot attend or who do not speak English. The Committee also will do what it can to assist in the preparation of English versions of papers submitted in other languages.

Persons interested in this conference are invited to send synopses of papers, or enquiries, to Dr. G. I. P. Levenson, Programme Convener, Research Laboratory, Kodak Limited, Harrow, Middlesex, England.

Personal Notes

Professor J. Eggert, Director of the Photographic Institute, E.T.H., Zürich, and an honorary member of the SPSE, has been named an honorary member of the Society of Scientific Photography of Japan.

Dr. Suzanne Bertucat, who assisted L. P. Clerc during 1959 until his death, has been named Editor of *Science et industries photographiques*. Through her efforts, this unique journal has continued publication without interruption.

Anwar Chitayat has been appointed Vice President of Engineering for Optomechanisms, Inc.

It is with deep regret that we learn of the death of Don Bennett on April 6, following a heart attack. Mr. Bennett served with distinction as Editor of the *PSA Journal* from 1952 until the time of his death.

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Discussion and Evaluation

Is There a Future for Photooptical Instrumentation for Metric Purposes in Missile Testing?

C. W. BEMISS, *RCA Missile Test Project, Patrick Air Force Base, Florida*

During the first ten years of missile testing, acquisition of metric data for determination of flight position, velocity, and acceleration information has depended to a large extent upon photooptical systems of various configurations. During this period of time, missile testing and evaluation ranges have met the requirements placed on them by airframe contractors to a surprising degree, considering that few of the systems were specifically designed for the task at hand. This has been accomplished only through application of a wide assortment of instrumentation systems of varying precision and reliability. Photooptical instrumentation has always been rated as a very dependable citizen in this community of data gatherers. Yet today, this same stalwart citizen is on the verge of being ostracized for furnishing data which is of marginal accuracy to meet current and future requirements and is available at too late a time to permit full utilization of its inherent value. The more stringent requirements dictated by our latest "refined" missiles and orbital vehicles for "all-weather" capability, greatly improved accuracy, and rapid delivery of data indicates a trend toward dependency on electronic systems unless a major "break-through" is achieved in the photooptical "state-of-the-art."

At present, photooptical acquisition of metric data is obtained from three basic systems. The first is the fixed precision sequential camera system employing the Bowen Ribbon Frame or CZR camera. Although this system is capable of a 10 sec of arc accuracy, usual operating accuracies range from 40 to 200 sec of arc, depending on mode of orientation, reference targets, and field operational conditions and problems. The results of a very recent study indicate that even a 5-sec arc accuracy might be achieved through utilization of a dimensionally stable base, development of an "optimum" process to inhibit emulsion swelling or adaptation of prehardened emulsions and close control of temperature and humidity in the film reading area.

The second system concerns tracking cameras such as the cinetheodolite. The potential angular accuracy of this instrument is 5 to 10 sec of arc, which is the random error of the existing system. Generally speaking, most operational ranges currently achieve accuracies of 15 to 35 sec of arc. The difference lies in systematic errors which can be eliminated. The utilization of higher frame or sampling rates in conjunction with second-degree polynominal velocity smoothing will also help obtain improved velocity and acceleration data accuracies. However, the achievement of higher accuracies is not simply the inclusion of more data points in a greater smoothing span, for an increased sampling rate does not decrease "bias" errors. Much has been said and much more work has been done on shaft digitization. Yet, to the best of our knowledge there is no "off-the-shelf" digitizer available which could be used with existing cine-theodolites, without degrading the accuracy of the instrument. For optimum performance, the least count of any digitizer equipment should be 1 sec of arc and the total error not more than 3 sec of arc. If a new tracking instrument were developed specifically for the launch phase of missile testing, the following characteristics and specifications would be very desirable:

a one-man remote tracking capability;

a 30-in. focal length folded optical system which could be converted to a 60 or 120-in. equivalent during a missile test;

a split optical system furnishing automatic tracking capabilities in conjunction with a film recording camera (For tracking purposes, the receptor might be a high-resolution video system, radiation tracking transducer, or electronic grid sensor.);

accurate shaft digitization with a least count of 1 sec of arc;

an automatic target acquisition system slaved to radar (Either aural or visual null would be acceptable.);

from 10 to 50 frames/sec sampling rate;

automatic exposure control;

1000-ft film magazines;

"timed" exposures;

and finally, the errors from all sources combined should represent less than 3 sec of arc.

The third photooptical system is one upon which we depend for the most accurate and precise position data. This is the ballistic camera system. With good data and a star calibration, the ballistic camera systematic error is significantly less than the standard deviation of the random error and probably ranges from one to two microns. This assertion is based upon a thorough system analysis and is supported by the residuals resulting from orientation calibrations and from triangulations. Even though it represents our most accurate recording capability, the ballistic camera system is still capable of being improved. Probably one of the weakest "links in the chain" concerns the ballistic camera plates. Although the optical system is capable of resolving 1 part in 200,000 and the photographic emulsion is coated on a plate which has been ground to a planarity of 6 fringes of light, the nonplanarity of the emulsion degrades the inherent capability of the optics and thus the over-all accuracy of the system. It is recognized that it is difficult to coat such a product as a glass plate and achieve a high degree

Presented at the National Conference, Chicago, 26 October 1959.
Received 7 January 1960.

of homogeneity in the emulsion as well as furnish a completely planar surface, yet this situation must be greatly improved if the photorecording facet of this problem is to complement the optical capabilities of the system. The second most prominent weakness of the ballistic camera system concerns the time delay in release of data after launch. It is suggested that the use of prehardened emulsions with rapid processing capabilities would be of material assistance. However, it must be borne in mind that any change such as development of a rapid process must retain the accuracy qualifications of the system or trend toward improvement of same. *There must be no degradation of the data.* The high precision of the ballistic camera system, and the fact that it is possible to associate meaningful estimates of accuracy with ballistic camera data, make this system a suitable standard for evaluating other range instrumentation. So much for improvement of accuracy with existing systems.

There remains, however, the need for operational improvement, particularly as it concerns rapid availability of processed and reduced data. As you are undoubtedly aware from public information coverage of missile testing, we are currently concerned with intermediate range and intercontinental range ballistic missiles and space probe launchings. These are only preliminary to space vehicle or space station launchings and satellite tracking requirements of the future. No longer is it acceptable to provide marginal capabilities in our instrumentation systems with delivery of reduced data a period of days to weeks after the launch. Instead, we must develop the most reliable and precise data system which will provide the necessary data within a period ranging from a fraction of a second to a maximum of a few hours. This is generally termed "real-time" or near-real-time delivery of data. The current photooptical systems usually require:

acquisition or exposure of data in the field;
transportation to a central facility;
laboratory processing of the record;
laborious manual reading of the record;
computer reduction, usually consisting of multiple passes with interim operator editing of results;
and finally, generation of reports and delivery of the data to the user.

Too often, it is not possible for the missile contractor to obtain the necessary data from one launch in sufficient time to permit program changes before the next test. *These conditions are no longer acceptable.* If not drastically improved, *this situation will be responsible for the demise of photooptical instrumentation for metric purposes in missile testing within the next three to five years.* However, it is not necessary to accept this as an eventuality, for application of known technical advances in the field of more rapid photographic processing and automated reading of data records will go far toward meeting these requirements. Thus, it should be possible to achieve "on-site" processing and reading of records with electronic transmission of digital data to a central reduction facility for "near-real-time" delivery of information. Such an arrangement has been recently developed for portable and remote operation of ballistic cameras to provide a global capability for orbital tracking.[1] A number of other proposed improvements in design and operation of the system are being strongly considered as one of the few known means of meeting the extremely stringent requirements of the future. Similar outstanding improvements should be sought for the other existing systems and consideration given to development of entirely new systems in such relatively unused regions as the infrared.

The photooptical industry has a splendid record of achievement for projects which it has undertaken, and it is believed that timely application of the best talent will provide a commendable answer to this challenge.

EDITOR'S NOTE

The need for improvement in optical instrumentation for missile and space vehicle tracking is discussed in another paper, recently published in *GSE* (*Ground Support Equipment*), 1:36–40, No. 3, Dec. 1959/Jan. 1960. In this paper, "Are We Falling Behind in Optical Instrumentation?", written by the *GSE* Executive Editor, Peer Fossen, the following areas of improvement are suggested: (1) Increase in range and accuracy of instruments. "Maximum range and accuracy can probably be achieved by ballistic cameras if the test ranges follow the example of the astronomers and utilize sophisticated large-aperture reflecting optics." (2) Achievement of real-time or near-real-time performance. "Telescope cinetheodolites show the greatest promise of achieving increased range and accuracy with real or near-real-time operation." (3) All-weather performance capability. This is one of the strongest advantages of electronic systems and can be realized by the use of airborne optical stations with infrared optical systems. Reasons which have kept the optical industry from realizing the necessary improvements are discussed and the relative capabilities of optical and electronic systems are evaluated. — *T. H. J.*

1. A. E. Glei, *Photogrammetric Eng.*, **25:** 381 (1959).

• Book and Journal Reviews

Electronic Flash Photography

A Survey of Principles and Practical Techniques in Industry, Research, and Radiography

RALPH L. ASPDEN, Macmillan, New York, 1960, 192 pp., $5^1/_2$ by $8^1/_2$ in., $8.50

This little book is tailored specifically for the scientist or experimenter who has a need for electronic flash techniques and wants to find out just what they are capable of doing. It manages to assemble in one place information scattered through a wide variety of technical journals.

In addition to describing the standard electronic flash unit such as is used by press and studio photographers, it discusses both single-pulse and cinema microsecond flashes, flash radiography, Kerr cells, spark sources and Schlieren photography, and even image converter tubes. One chapter is devoted to circuitry and tube designs to produce various combinations of intensity and duration as well as allow repetitive flashing. Another chapter is devoted to photographic considerations, reciprocity-law failure, and the types of spectra and continuous emission developed by these tubes over ranges of loading.

A section on various practical problems solved with flash techniques is particularly interesting as the author is responsible for high-speed photographic research and development at the Royal Aircraft Establishment in England. Illustrations are included showing birds and insects in flight, propeller action in both air and water, sprays, projectiles, and rain erosion as found on missiles or high-speed aircraft.

This is a survey, not a textbook, and confines itself to general considerations rather than specific characteristics, derivations, or working circuits for a particular design. There are, however, many simplified electrical schematics covering all general classes of power supplies. Since this is an English book, equipment selected for discussion is that generally available in England. Some of the commercial units shown are not familiar on the American market.

The book has 100 illustrations and diagrams, is indexed, and contains an excellent bibliography.—*H. G. Morse, Ansco, Binghamton, N.Y.*

Fundamentals of Photographic Theory

T. H. JAMES AND G. C. HIGGINS, 2nd ed., Morgan and Morgan, Inc., New York, 1960, 345 pp., illus., $5^3/_4$ by $8^1/_2$ in., $7.50

College educators, and other persons utilizing photographic theory concepts, will be pleased to learn that *Fundamentals of Photographic Theory*, by Drs. James and Higgins, is again in print and in the form of a second edition. The original text has been revised to include a wider coverage of subjects and important advances.

Material on emulsion preparation has been increased to include additional information in such areas as silver iodide, physical ripening, after ripening (chemical sensitization), and low-gelatin emulsions for nuclear particle recording. Latent-image theory includes a well-prepared section on physical imperfections in silver halide crystals and a clear presentation on energy bands in silver halide crystals. New sections on the effect of an electric field on the shift of latent-image centers and modifications of Gurney-Mott Hypothesis, including Mitchell's Mechanism, serve to show how this edition has been modernized. The chapter on the mechanism of development has enlarged sections on silver catalysis and direct development, with new sections on the charge effect relative to initiation of development and on solution-physical development. Comparative electron micrographs on post-fixation physical and solution-physical development are included.

Those persons particularly interested in color photography will find new material on secondary color development and color densitometry. The latter is a brief description involving terminology and basic concepts. The inclusion of sensitometric evaluation of color data would give further strength to this phase of the book.

Phenidone's structure, its rate dependency on bromide concentration, and classification as a developing agent are presented. Further information is included on the effect of concentration, alkali, and temperature on the rate of development. Cationic development accelerators, superadditivity and classification of developing agents structure relative to kinetics, fine-grain development, and latensification are included as new material. Hypersensitization is not included.

The discussion of speed determination has been enlarged and includes the newly accepted ASA standard. Recent sensitometric comparisons involving the use of the exposure value system, vector parameter, and statistics are described and explained.

Perhaps the most important expansion of this edition is the section on the structure of the developed image. The excellent discussion brings together the basic concepts and explains them in a most lucid manner. Those concerned with image evaluation will find the added information on turbidity, sharpness, acutance, spread function, resolving power, edge trace, and sine-wave response of great value.

The authors have again displayed an exceptional ability to offer highly technical photographic concepts in a well-organized and clear manner. To those who wish to be currently informed in the field of photographic theory, this book is strongly recommended.—*William S. Shoemaker, Rochester Institute of Technology, Rochester, N.Y.*

Zhurnal Nauchnoĭ i Prikladnoĭ Fotografii i Kinematografii

Vol. 4, No. 5, September-October 1959 (in Russian)

Résumés by S. C. Goddard

[*Abstracts of pp. 321-383 in the Sept.-Oct. issue of* Zhur. Nauch. i Priklad. Fot. i Kinematografii *appeared in the last issue of* Phot. Sci. & Eng.]

The Isothermal Development of the Layers of [Nuclear] Emulsions

SAMOĬLOVICH AND E. S. BARINOVA (Letter to the Editors), pp. 383–384

The best conditions for the isothermal development of NIKFI R and another similar Soviet nuclear emulsion

have been studied. The results are set out in tabular form and the recommended conditions are: type of development, 2.5–4 hours, pH 6.7–7.0, temperature 8° – 10°.

A New Method of Determining the Brittleness of Photographic Films

F. S. SHERMAN, pp. 389–392

A description is given of P. Z. Adelstein's wedge brittleness test for photographic film (*Phot. Sci. & Eng.*, **1**: 63–68 (1957)).

Conference on the Basic Problems in the Theory and Technology of the Color Photographic Processes

S. A. BOMGARD, pp. 393–399

Abstracts are given of 28 papers presented at a conference organized by the Commission for Scientific Photography and Cinematography of the Academy of Sciences of the USSR in collaboration with NIKFI and No. 3 Film Factory, 29 May – 1 June 1959. The subjects discussed were the manufacture of multilayer color photographic materials (9 papers); the sensitometry of color photographic processes (5 papers); color production in the photographic processes (4 papers); and imbibition printing (7 papers).

Modern Infrared Sensitive Materials

S. M. SOLOV'EV, pp. 385–389

A comparison is made of the sensitometric properties of a number of infrared films and plates available on the international market. The results of the comparison are tabulated.

Review of Work of Young Scientific Workers at NIKFI

V. G. ZHIRYAKOV, pp. 399–400

Brief reports are given of the papers presented at a special conference of the Research Institute, devoted to the work of its younger scientists.

Zhurnal Nauchnoĭ i Prikladnoĭ Fotografii i Kinematografii

Vol. 4, No. 6, November-December 1959 (in Russian)

Résumés by S. C. Goddard

Study of Factors Influencing the Intensity of the J-Bands in the Absorption Spectrum of Aqueous Gelatin Solutions of Dibenzothiacarbocyanine Dyes

A. V. BORIN, P. N. ZALEZNYAK, AND I. A. POBEDONOSTSEVA, pp. 401–410

The maximum intensity of the J-bands has been observed for two concentrations of gelatin (0.01 and 5–10%) in 4×10^{-5} *M* dilutions of 3,3'-dimethyl-9-ethyl-4,5,4',5'-dibenzothiacarbocyanine chloride. The concentration of chlorides in the gelatin had no significant influence on the intensity of the J-bands. The J-band is significantly strengthened in solutions containing gelatin which has been freed from disaggregated fractions. Technological factors in the manufacture of the gelatin leading to its disaggregation cause a weakening of the J-band in dye solutions of the gelatin. Some suggestions are made on the mechanism of the action of the factors studied on the intensity of the β- and J-absorption bands.—(*Adapted from authors' abstract*)

Electrical Conductivity of Gelatin and Its Variations with Illumination

L. G. GROSS, pp. 411–416

The temperature coefficient of the electrical conductivity of gelatin at room temperature is approximately 10%. The observed changes in the conductivity of the gelatin under the action of light and infrared radiation were due to heating of the sample, and consequently it has no importance for the problem of the light sensitivity of photographic materials. The optimum humidy found in Kamiya's work (*J. Chem. Soc., Japan, Pure Chem. Sec.*, **75**:788 (1954)) is observed when the resistance of the sample and the input resistance of the d-c amplifier are equal.—(*Translation of author's abstract*)

The Kinetics of Development of Separate Tracks of Ionizing Particles in a Photographic Layer. I. Differences in the Kinetics of Development as a Consequence of Differences in the Dimensions of Development Centers

A. L. KARTUZHANSKIĬ, pp. 417–422

A study has been made of the kinetics of development of tracks of particles of different ionizing powers on layers with different sensitivities, which appear to be quite similar to the kinetics of development of a continuous density formed by the action of particles: with a decrease in the ionizing power of the particles and sensitivity of the layer, development is delayed as a result of the diminution in the dimensions of the centers forming the latent image. Variations of a few (<5) atoms of silver in the dimensions of the centers are capable of producing a significant change in the kinetics of development.

A determination has been made (on the basis of reciprocity failure) of the minimum dimensions of a development center, n_0, for all the emulsions studied with different times of development. A linear relation between $1/n_0$ and the time of development was confirmed.

Comparison of the number, n, of secondary electrons, formed by the particles on passing through a silver halide crystal in different emulsions, with the number of silver atoms in the development center, n_0, for the same conditions of development, has allowed the approximate estimation of the number of such centers in the crystal, the loss of secondary electrons in the formation of the latent image, and the relation between these losses and the speed of the emulsion.—(*Translation of author's abstract*)

Antirepellency Activity of Wetting Agents in the Coating of Photographic Emulsions. III. Antirepellency Activity of Sulfosuccinic Esters and Their Influence on the Kinetics of Wetting

O. K. SMIRNOV, S. M. LEVI, AND K. O. AVERBAKH, pp. 423–426

Eight dialkyl esters of sulfosuccinic acid were prepared and evaluated for their antirepellency activity in the coating of an emulsion prone to repellency trouble. The wetting agents were used in quantities of 2.5, 5, and 10 ml of 0.1 *M* aqueous solution in 1 liter of emulsion. It was found that the antirepellency activity reached a

maximum when the total number of carbon atoms in the two alkyl chains was twelve to sixteen. Best results were obtained with the sodium salt of dihexylsulfosuccinate. Comparison with the wetting agents studied in the two earlier parts of this series (*Zhur. Nauch. i Priklad. Fotografii i Kinematografii*, **3**:34, 416 (1958)) shows the present series to be active at lower concentrations.

Relation Between the Sensitivity of Nuclear Emulsions and Temperature in the Range 2–300°K

V. A. BELYAKOV, L. G. KOZLOVA, V. A. SVIRIDOV, AND K. D. TOLSTOV, pp. 427–429

Curves are given to show the variation of the speed of NIKFI-R 400-μ emulsion with temperature, both for normal processing and for an enhanced development. The latter gives some over-all increase of speed. The curve for Ilford G emulsion, using the processing conditions recommended by the manufacturers, is given for comparison. A NIKFI emulsion without iodide, made especially for nuclear-particle work at low temperatures, has given an improved performance at 20°K, reaching a track density of 17 grains per 100 μ. However, this emulsion shows considerable batch-to-batch variation.

Scattering of Light by Opal Glasses and Their Use in Densitometry

V. A. KORNDORF AND I. H. CHERNYĬ, pp. 430–432

The Russian sensitometric standard, GOST 2817-50, specifies that the densities of a step wedge should be read with the emulsion surface in contact with an opal glass, the thickness of which should be such that no increase in it will influence the results. This specification was considered to be inadequate, in view of the different properties of different opal glasses. Accordingly, a study was made of the light-scattering properties of a number of Soviet-produced opal glasses, together with one foreign one, and an opal plastic. The angular distribution of scattered light from the opal glasses is tabulated.

A Study of the Possibility of Increasing the Photographic Speed of Panchromatic Films by Means of Cyclic and "Starved" Development

K. I. MARKHILEVICH AND V. L. ABRITALIN, pp. 433–437

High-speed panchromatic films give their best detail-rendering with a gamma of 1.7, but when developed to this gamma, some films show speeds three to four times below the nominal. In order to raise the film speed while developing to this particular gamma, cyclic and "starved" development have both been tried. In cyclic development, the film is passed through the developer, rewound, and left for a short while, this cycle being repeated as often as required (in this case three times). For a given gamma, the speed was raised by this method 20 to 40% in comparison with normal development. In addition, the film was developed more uniformly along its length. "Starved" development consists in soaking the film until saturated in the developer at a low temperature, removing it, and leaving it until development is complete. This form of development gave an increase in speed of about twice for a given gamma. The latitude of the film was also increased approximately twice, and there was an increase in the maximum density. Recommended formulas for starved development are given.

An Apparatus for the Automatic Adjustment of the Lens Diaphragm of an Aerial Camera

N. A. BELYAEF, pp. 438–445

Aerial photographic testing of the aero camera K-17B with the apparatus for automatic adjustment of the lens diaphragm (ADO) at heights of 300-3000 meters, carried out in 1955 and 1957, has shown that the ADO apparatus is simple to control, reliable in working, and normally ensures automatic adjustment of the diaphragm of the aero camera lens according to the average brightness of a locality with the usual variegated appearance, under various conditions of lighting during the summer and autumn working day. The average integral density of negatives was maintained around the average normal value over different frames of the aero film obtained under conditions of automatic adjustment of the lens diaphragm of the aerial camera, with different lighting conditions and also in the presence of cumulus clouds. Measurements of the density of negatives departed from the mean density value of the film by quantities of the order of $\pm$ 0.05 for individual frames, which is close to the projected accuracy of working of the ADO apparatus.—(*Translation of author's abstract*)

Some Photometric Characteristics of Winter Aerial Landscapes

N. A. TEPLYAKOV, pp. 446–457

The photometric properties of winter (snow-covered) landscapes have been studied from the air with a photoelectric telephotometer. The outstanding features of these landscapes are the wider brightness range compared with that of a summer landscape, coupled with the low contrast of detail. The situation is complicated by the relative absence of intermediate tones, the overwhelming majority of elements of detail occurring in the highlights and shadows, i.e., on the shoulder and toe of the characteristic curve, where resolving power is low. The integrated brightness differs widely for different types of landscape; hence, it is wrong to use a single average figure for brightness in making exposure calculations. All these considerations point to the necessity for using a film with much greater latitude than usual and for taking particular care over estimating the exposures required. The results obtained in the investigation are set out in detail.

Influence of Wetting Agents on the Photographic Properties of Light-Sensitive Layers

A. V. BORIN (Letter to the Editors), pp. 458–459

The surface-active agent, octadecenylpolyglycol ester, having the structure $H–C_{18}H_{35}(CH_2–CH_2O)_{80}H$, when added to a nonsensitized, high-speed ammoniacal emulsion increased the natural sensitivity, and, when added to the same emulsion sensitized with 3,3′-diethyl-9-ethyl-4,5,4′,5′-dibenzothiacarbocyanine chloride gave an increase in both the natural and the conferred sensitivity, the effect being more marked when the wetting agent was added before the introduction of the optical sensitizer into the emulsion. A similar effect was obtained when the emulsion was sensitized with a 5,5′-disubstituted 9-ethylthiacarbocyanine. Digestion tests with a gold-sensitized emulsion showed that the presence of the wetting agent increased the maximum speed above that of the gold sensitization alone.

The Energy Range of the Exciton Band in Silver Bromide

S. G. RYZHANOV (Letter to the Editors), p. 460

The top of the exciton band in silver bromide is known to be about 0.01 ev below the bottom conduction level. The author considers that the hypothesis put forward by Goodeve and Kitchener (1938), according to which the sensitivity of a silver bromide emulsion sensitized by a dye is determined by an exciton mechanism, has more support from experiment than the Gurney-Mott theory. He concludes that the distance between the top of the unexcited bands of the silver bromide cyrstal and the bottom of the exciton band is about 1 ev. Hence the exciton band occupies more than half of the forbidden zone of the crystal, which for silver bromide is about 2.5 ev.

A Variant of the Electrophotographic Process

P. M. PODVIGALKIN (Letter to the Editors), pp. 461–462

In order to overcome some of the disadvantages in present forms of electrophotography, namely, the necessity of using a source of very high potential and semiconductors with a very high resistance, the author has devised a new method. In this, the light-sensitive element consists of a semiconducting layer (amorphous selenium) coated on glass covered with a film of lead dioxide. The plastic surface of a polystyryl-coated paper is brought into contact with the semiconducting layer by the pressure of a metal plate. This plate and the lead oxide layer form two electrodes to which is applied a potential of 400 to 600 v. Exposure is made through the glass, as a result of which a latent electrostatic image is formed on the insulating plastic layer. This occurs only when the lead oxide electrode is negative. The paper is then separated from the semiconducting layer and developed in a liquid developer (a printing ink in benzene). A negative image is obtained, since the potential on the paper is higher in the exposed areas than in the unexposed. The author proposes a theoretical explanation of the process, which is regarded as being only in an experimental stage.

Measurement of the Distortion of Particle Tracks in Nuclear Emulsions Developed by Different Methods

D. M. SAMOĬLOVICH AND V. A. SMIRNITSKIĬ (Letter to the Editors), pp. 462–463

Measurements made on Soviet nuclear emulsions are tabulated.

On the Influence of Some Chemical Sensitizers on the Dispersion and Light Sensitivity of Ultrafine-Grain Emulsions

I. A. NOVIKOV AND N. S. GAFUROVA (Letter to the Editors), pp. 463–64

Curves showing the change in mean grain size and in speed for different types of digestion have been obtained on an ultra-fine-grain emulsion sensitized with a gold thiocyanate—potassium thiocyanate complex salt, and with its separate components, namely, chlorauric acid and potassium thiocyanate. The chlorauric acid had little effect on the decrease in dispersion on ripening, but more influence was shown by the gold thiocyanate. All the substances studied increased the speed of the emulsion, the gold thiocyanate complex having the greatest effect on both the speed and the grain size. Other experiments have shown that sodium thiosulfate increases the speed of the emulsion but does not influence the change in dispersion. It is concluded that, in the case of gold-sensitization, the increase in speed is due to the increasing grain size as well as to chemical sensitization.

The Application of the Fourier Integral to the Study of the Properties of the Optical and Photographic Image. I. The Optical Image

A. T. ASHCHEUNOV, pp. 465–476

A review.

Russian Patents on Electrophotography

Translations by S. C. Goddard of abstracts published in Tekhnika Kino i Televideniya, Vol. 3, July 1959

A Method of Preparing Radiographic Anaglyphs

I. I. ZHILEVICH, Avt. Svid. (Russ. Pat.) 111447, filed 5 November 1956.

Radiographic anaglyphs are obtained by projecting two images at different angles of projection, developing with dyes, and intensifying them on the same photoconducting layer of an electrophotographic material charged twice.

Developing Powder for Electrostatic Projection Printing

V. M. FRIDKIN, T. N. GERASIMOVA AND KH. S. BILYALETDINOV, Avt. Svid. 112645, filed 5 April 1957

In a developing powder consisting of a mixture of finely reduced particles of natural or artificial resins with coarser particles of "carrier," the carrier used has different sized particles, 0.1 – 0.3 mm and 0.5 – 0.7 mm.

For preparing the developer 1.5 – 2 parts by volume of a developing mixture consisting, for example, of estergum 32% (by weight), asphalt 32%, colophony 27%, bitumen-lac 6%, and spirit nigrosine 3% are mixed and carefully ground in a mortar with 5 – 6 parts by volume of a coarse (0.5 – 0.7 mm) sand. To the mixture so obtained is added 5 – 6 parts by volume of a fine sand (0.1 – 0.3 mm) and this is mixed in without grinding.

On treating the latent electrostatic image with such a mixture, the developing powder is transferred from the coarser to the finer particles of the carrier. The resin particles settle on those parts of the image bearing a charge opposite in sign to the charge on the developer, thus giving a positive image. Excess of developer particles is retained by the fine sand and completely eliminated from background areas.

Photo-Semiconducting Material for Electrophotography

I. I. ZHILEVICH, Avt. Svid. 112922, filed 16 November 1956.

There is proposed a material for electrophotography which preserves the electrostatic charge imparted to it for an extended period. The material consists of a thin metallic strip (e.g., aluminium foil) on which a conventional photoconducting layer is coated on one side and on the other a thin dielectric layer exhibiting a dielectric permeability and a volume specific resistance exceeding the corresponding dark characteristics of the photoconducting layer.

As electrification of the layer proceeds the film is wound into a tight roll. A considerable part of the electric charge is then concentrated on the capacitance formed by

the base, the dielectric, and the surface of the photoconducting layer, bringing about a lowering of the over-all potential difference and a slowing-up of the discharge process. The potential rises again as the film is unwound before exposure.

Material for Electrophotography

I. I. ZHILEVICH, Avt. Svid. 114634, filed 29 September 1956.

A method is proposed for preparing materials for electrophotography by using semiconductors showing a strong photoelectric effect, but having a color differing from white. For this, onto the base is coated a bottom layer with a strong photoelectric effect, e.g., a suspension of 6 g cadmium sulfide in 45 ml of a solution of one part by volume of BF-2 cement in two parts of ethyl alcohol, and a top, thinner, layer with a white color, e.g., a suspension of 12 grams zinc oxide in 50 ml of the above solution of BF-2 cement in alcohol. The zinc oxide has a high covering power and its whiteness almost completely compensates for the yellowish-brown color of the surface of the bottom layer.

The relative light sensitivity of the combined material so obtained is expressed as 37.7. At the same time the relative sensitivity of the separate cadmium sulfide suspension coated under the same conditions is 64, and that of the zinc oxide suspension 4.7.

A Method for the Separate Development of the Individual Parts of a Latent Electrophotographic Image

S. M. KHAZAN, Avt. Svid. 115933, filed 3 June 1957.

When the developer is applied through a grid electrode placed between the container and (electrophotographic) layer being developed, the potential being changed during development, it is possible to obtain a multitone (polychrome) image on a singly exposed layer, using for this developers of different tones (colors).

In practice the method may be carried out by means of known apparatus for the development of electrostatic images, e.g., with the aid of apparatus consisting of an inverted conical reservoir, in the apex of which is situated a rotating brush which throws out onto the surface of the semiconductor particles of developing powder charged to a determined potential by the action of the triboelectric effect.

Meanwhile the grid placed in front of the photoconducting layer is given the same charge, so that the powder is precipitated only on determined parts, e.g., in the darker portions of the image, development being carried out with, e.g., a black powder. The potential of the grid is lowered and intermediate tones are developed, and finally, after still further lowering the grid potential, highlights are developed, e.g., with a light brown powder.

The multitone image obtained in this way is transferred in the usual manner to a permanent base or fixed directly on the semiconducting layer.

A Material for Electrophotography

R. S. NAKHMANSON, Avt. Svid. 116811, filed 29 March 1958.

In order to extend the spectral working region of electrophotographic materials and increase their speed to long-wave radiation, a sensitive layer is made from a ferro-electric material. The following sequence of operations is recommended for photography with this material. Onto the film is focused the object to be photographed, as a result of which the individual parts of the layer, with different temperatures, attain different dielectric permeabilities. The layer is charged by means of a corona discharge in air, after which the high potential is removed with the corona electrode and the exposure is terminated. The temperature, and consequently the dielectric permeability, of the ferro-electric layer then becomes equalized, and the surface assumes a potential relief which is developed by the usual methods.

Electrophotographic Copying Apparatus

I. V. ANFILOV, V. M. FRIDKIN AND YU. N. BARULIN, Avt. Svid. 117038, filed 18 April 1958.

A description is given of an electrophotographic copying apparatus for the duplication of plans and drawings on photoconducting paper, consisting of a charging device, an exposing unit in the form of a transparent cylinder inside which is placed a light source, a device for development consisting of two containers and a mechanism for conveying the developing powder from the lower container to the upper, and apparatus for reinforcing the developed image. Between the container and the mechanism for conveying the developing powder from the lower container is a band conveyer passing over four rollers forming a rectangle. The purpose of the conveyer is to distribute the powder uniformly over the width of the upper container.

Electrophotographic Enlarger for Oscillograph Traces

I. I. ZHILEVICH, Avt. Svid. 116107, filed 5 March 1958.

An electrophotographic enlarger for oscillograph traces consists of an optical system which projects the image to be reproduced from a continuously moving film onto a previously charged photoconducting band, the latter being drawn through a vessel with developing fluid by a system of rollers.

A Method of Preparing [Electrostatic] Photographic Prints

V. S. MAGNITSKII, Avt. Svid. 117454, filed 12 December 1957.

A method of [electrostatic] photographic printing with density compensation by masking is claimed. The mask is obtained on a transparent electrophotographic layer by projecting onto the layer a negative image with subsequent development of the latent image in the electrostatic layer. Since the powder may be easily removed from the surface of the electrophotographic layer, masks for several negatives may be obtained on the same electrophotographic plate.

Brochures

Résumé by Frank Smith

"Kodak Materials for Aerial Photography"

The 42-page booklet, "Kodak Materials for Aerial Photography," has been revised and brought up to date to include new films and materials designed for this specialized field. It may be obtained from the Eastman Kodak Co., Rochester 4, N.Y.

PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 4, Number 3, May-June 1960

• New Products and Developments

FRANK SMITH

• Cameras and Accessories

Lallemand Electronic Camera at Lick Observatory

An electronic camera designed by Prof. Andre Lallemand of the Paris Observatory has been used in conjunction with the 120-in. telescope of the Lick Observatory to make spectrograms of Spiral Nebula M31. The spectrograms show that the nucleus is rotating faster than the outer portions, a fact not previously known. The results indicate that stars at a distance of 25 light years from the center of M31 make a complete trip around the galactic center every million years.

In the electronic camera, the light from the 120-in. telescope is imaged on a photoelectric cathode of high sensitivity. As an example of the camera's effectiveness, the spectrograms of M31 required exposures of 15 to 45 min. With the same spectrograph and the best photographic plates available, an exposure of 5 to 15 hours would have been required.

Benson-Lehner Ellis Ultra-Speed Camera

An ultrahigh-speed camera system developed by Dr. Albert T. Ellis of the California Institute of Technology is now being manufactured by Benson-Lehner Corp., 1800 Franklin St., Santa Monica, Calif. Called the Ellis Ultra-Speed Camera, it consists of the camera, camera control, lighting control, and electronic flash lamp. The Kerr Cell shutter unit is made up of two polarizing filters, one on either side of a 1½-in. diameter cell containing nitrobenzene, and two nickel electrodes which produce a controlled electric field. After the light rays pass through the shutter, two lenses transmit the image to a rotating mirror at the center of the circular film box. The 35mm film is located along the periphery of the box. The rotating mirror is a wedge-shaped piece of nickel-plated aluminum, attached with its face at an angle of 45° to the shaft of a variable-speed compressed-air turbine having a maximum speed of 100,000 rpm. The mirror images the light rays on the stationary film.

Illumination is provided by a GE Type-FT623 Flash Lamp. Framing rate of the camera is 480 to 1,600,000 pictures/sec.

Robot Star II Automatic 35mm Camera with Double Motor

The Robot Star II, a 35mm camera with a double internal spring motor for automatic film transport, shutter cocking, and exposure count, for taking up to 55 automatic exposures without rewinding, is being distributed by Karl Heitz, Inc., 420 Lexington Ave., New York 17.

Equipped with a large 1:1 viewfinder, it offers interchangeable Schneider lenses from 30mm up to 150mm. The all-metal rotary shutter provides speeds from ½ to $\frac{1}{500}$th sec and B, with both M- and X-synchronization at all speeds. The 24 by 24mm size of the frames give 30 exposures from a standard 20-exposure or 55 exposures from a 36-exposure roll. The camera accepts all standard 35mm cartridges as well as the Robot bulk loading and take-up cassettes.

The Robot II can be supplemented by electromagnetic remote release, camera holder, timers, etc., for application to scientific and industrial photography.

• Illumination

Beckman and Whitley Electronic Flash for High-Speed Photography

An electronic flash unit, Model 357, has been developed by Beckman and Whitley, Inc., San Carlos, Calif., to meet the specific needs of high-speed framing cameras providing exposures down to 1 μsec. The unit has a capacity of 1200 w-sec, and delivers a single square-wave light pulse whose duration is controllable to correspond to the writing rate of the camera. Duration settings are 8.70, 11.15, 14.75, and 22.25 msec. Rise and decay times of the pulse are approximately 40 μsec.

The unit can be triggered from any of the following: normally open or normally closed switch, positive pulse, or photoelectric cell. An additional feature is a modeling lamp which operates at 60 flashes/sec for use in framing, focusing, and positioning of lamps. Operation is from a 115-v 60-cps 5-amp integral power supply.

• Optics

Elgeet Cathode-Ray Lens

The Navitar, a 6-in., *f*/1.9 lens for high-resolution one-to-one transfer of information from cathode-ray tubes, has been announced by Elgeet Optical Co., Inc., Rochester, N.Y. The lens has been designed to work in the range of 4200–6000 A, peaked at 4300 A, which is near the region of maximum output of the P-11 phosphor. The lens operates at one-to-one in an object-to image distance of 22.370 in., but can also be used at a magnification of 1:1.125. While covering a diagonal of 4.500 in., the iris is adjustable from *f*/1.9 to *f*/16, and has been designed with a gear so that it may be mated with remote adjustment mechanisms. Over-all length of the lens is 5¾ in. and maximum diameter is 4 in.

ARC Telefold Lens

A lens-mirror system called the Telefold has been developed by Atlantic Research Corp., Alexandria, Va. The design provides a long focal-length system in a short lightweight package. Diameters up to 12 in. and focal lengths up to at least 200 in. can be supplied. The

Although the information contained in this section is compiled from sources believed to be reliable, the author cannot assume responsibility for its accuracy. Publication of the information here is not to be construed as an endorsement or recommendation of the product or equipment described.

prototype model is a 50-in. focal-length $f/14$ unit, 4 in. in diameter and 10 in. long, weighing 2¼ lb. The lens may be adapted to many 8mm, 16mm, and 35mm still or motion-picture cameras.

The lens may be used as a telescope with powers up to 150× by adding an eye piece and an erecting system. A finder telescope can be mounted on either side of the lens. Accessories include a combination lens shield and dew cap, and filters for solar work.

Traid Wide-Angle Lens for Prism Cameras

The Traid 120 lens with an acceptance angle of 165°, for use with the Photo-Sonics 16mm - 1B High-Speed Camera has been announced by Traid Corp., 17136 Ventura Blvd., Encino, Calif. The 3.53mm focal-length lens with stops of $f/1.9$ to $f/16$ is 3.20 in. in diameter and 5.86 in. long, and weighs about 2 lb. It uses coated optics, color corrected for the visual region, and is provided with clear and haze filters.

50mm f/0.519 Lens

According to a brief technical note appearing in the March 1960 issue of *Modern Photography*, Shotoro Yoshido of the Science Laboratory Sendai, Japan, has designed a 50mm $f/0.519$ lightweight well-corrected five-element lens of high resolution. The design uses a thin aspheric front element instead of an element with a deep symmetrical curve. It is claimed that spherical and chromatic aberrations are almost completely absent, and that astigmatism, coma, distortion, and curvature of field are minimized.

• Miscellaneous

Wihtol Recording Microphotometer

A recording microphotometer, Model DB-3, developed by Wihtol Industries, Eatontown, N.J., has been designed to accommodate either glass plate or film photographs, and, together with the M-H Electronic Recorder, it provides for continuous analysis of photographic images. Features of the unit are: rigid castings to support and align the scanning lamp and lens system; scanning lamp with variable voltage control; micro-adjustment for phototube and aperture mount; four fixed carriage speeds; and interchangeable apertures permitting use of either pinhole or slit openings. Overall dimensions of the unit are 18 by 26 by 18 in.

CEC Modular Recording Oscillograph with Rapid Printout

The Type 5-123 Recording Oscillograph developed by the Electro-Mechanical Instrument Div. of Consolidated Electrodynamics Corp., 360 Sierra Madre Villa, Pasadena, Calif., can be built to a variety of configurations by the assembling of mounting, record drive, optical drive, and front panel control modules. Although 36 and 50 channels will be basic, other sizes are possible by changing magnet blocks in the optical module. Record speeds from 0.1 to 160 in./sec are provided by the drive module. Capacity is 475 ft of 12-in.-wide thin-base paper.

Used with the oscillograph is a rapid printout technique called Dataflash, in which the record passes over a heated platen as it is flooded with bright light. The clear dry record is produced in less than 1 sec.

AVCO Optical Fiber System for Dental and Medical Use

A new instrument that permits a dentist to view any part of a patient's mouth, highly magnified, on a television screen has been demonstrated at the U.S. Navy Dental School, Bethesda, Md., according to a joint announcement by the Navy and Avco Corporation, 201 Lowell St., Wilmington, Mass.

The device, which uses an optical fiber probe linked to a closed-circuit television system, can eventually be adopted for medical probes to explore inside the human body.

The optical system consists of a bundle of optical fibers bound together in a small whip-like cable with a fingertip-size lens arrangement at the probing end and coupled to a closed-circuit television camera at the other end.

A bundle contains up to 10,000 of the hair-like fibers. Each tiny fiber picks up light from a microscopic section of the surface in front of it and transmits it to the other end. With thousands of the fibers bound tightly into a cable, a picture made up of the thousands of light segments can be sent from the lens inside the patient's mouth to the television camera and from there to the screen, where the tooth or a portion of it, is seen magnified up to 35 times.

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